이학박사학위논문

Cu-Catalyzed Multicomponent Polymerization: Library Synthesis Based on Diversity-Oriented Polymerization

구리촉매를 이용한 멀티컴포넌트 고분자 중합법 : 다양성을 기반으로 한 고분자 라이브러리 합성

2017 년 2 월

서울대학교 대학원
화학부 고분자화학 전공
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지도교수 최 태 림

이 논문을 이학박사학위논문으로 제출함

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김현석의 이학박사 학위논문을 인준함.

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Abstract

Cu-Catalyzed Multicomponent Polymerization: Library Synthesis Based on Diversity-Oriented Polymerization

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Constructing well-defined polymer structure with simple protocol is the all-desiring issue in synthetic chemist. Especially, multicomponent polymerization is one of the challenging field because it generally suffers from defect and low molecular weight oligomers due to lack of perfect orthogonality among monomers. Following three chapters describe successful Cu-catalyzed multicomponent polymerization, providing extreme efficiency with high selectivity and simple synthetic protocol.

Chapter 2 describes preparation of a library of poly(*N*-sulfonylimidates) by using three kinds of monomers. (diyne, sulfonyl azides, and diols) New synthetic polymers were prepared just by changing single monomer family. Formation of polyimidates is highly selective over conventional click reactions and overcomes the drawbacks of general multicomponent polymerizations showing narrow monomer scope and low-molecular weight polymers. Furthermore, applying easy-accessible and bench stable diol, this polymerization opens up the possibility of huge combination of multicomponent polymers.

Chapter 3 provides an efficient and step-economical synthesis of various graft and dendronized polymers by Cu-catalyzed multicomponent polymerization. In this chapter, we accomplished unity of multicomponent systems divided into two preparations (polyamidines and polyimidates) and expanded this method to higher dimension of microstructure of polymer with perfect orthogonality. 54 different high-molecular-weight graft and dendronized polymers were prepared from 11 diamines, 3 diols, 6 bis-sulfonyl azide, and 14 macromonomers containing mono-alkynes (4 linear polymers and 10 dendrons). With this route, complex polymer architectures were synthesized in one-shot reaction, allowing simultaneous adjustment of the main backbone and the side chains.

Chapter 4 describes synthesis of multi-graft polymers by graft-to stategy. By using this method, different side chains or dendrons could be tethered on the single polymer chain. Two distinct

mono-functionalized macromonomers enriches polymer architectures and properties, paving the way easy synthesis of future functional materials.

keywords : Cu-catalyzed multicomponent polymerization, Library synthesis, one-shot synthesis, polyimidates, graft, dendronized polymer

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Abbreviations and symbols

AFM	atomic force microscopy
DIPEA	*N,N*–diisopropyl ethylamine
DMSO	dimethyl sulfoxide
DMF	*N,N*–dimethyl formamide
DP	degree of polymerization
EtOAc	ethyl acetate
Equiv	equivalent
FT–IR	Fourier transform infrared
FAB–MS	fast atom bombardment mass spectroscopy
HRMS	high resolution mass spectroscropy
IR	infrared
MALDI–TOF	matrix assisted laser desorption ionization–time of flight–mass spectrometry
mp	melting point
NMR	nuclear magnetic resonance
PDI	polydispersity index
ppm	part per million
RT	room temperature
SEC	size exclusion chromatography
TEA	triethylamine
TPA	tri–n–propylamine

TBA	tri−n−butylamine
TOA	tri−n−octyllamine
THF	tetrahydrofuran
UV−Vis	ultraviolet−visible
TEM	transmission electron microscopy

Chapter I

Introduction to Multicomponent Polymerization

1. Introduction

Step-growth polymerization for building AB sequences has great advantage for preparing functional polymers. Since Carothers synthesized Nylon by this polymerization, many polymers arise from different type of organic reactions. Also, diverse synthetic methods can converge to one polymer preparation.

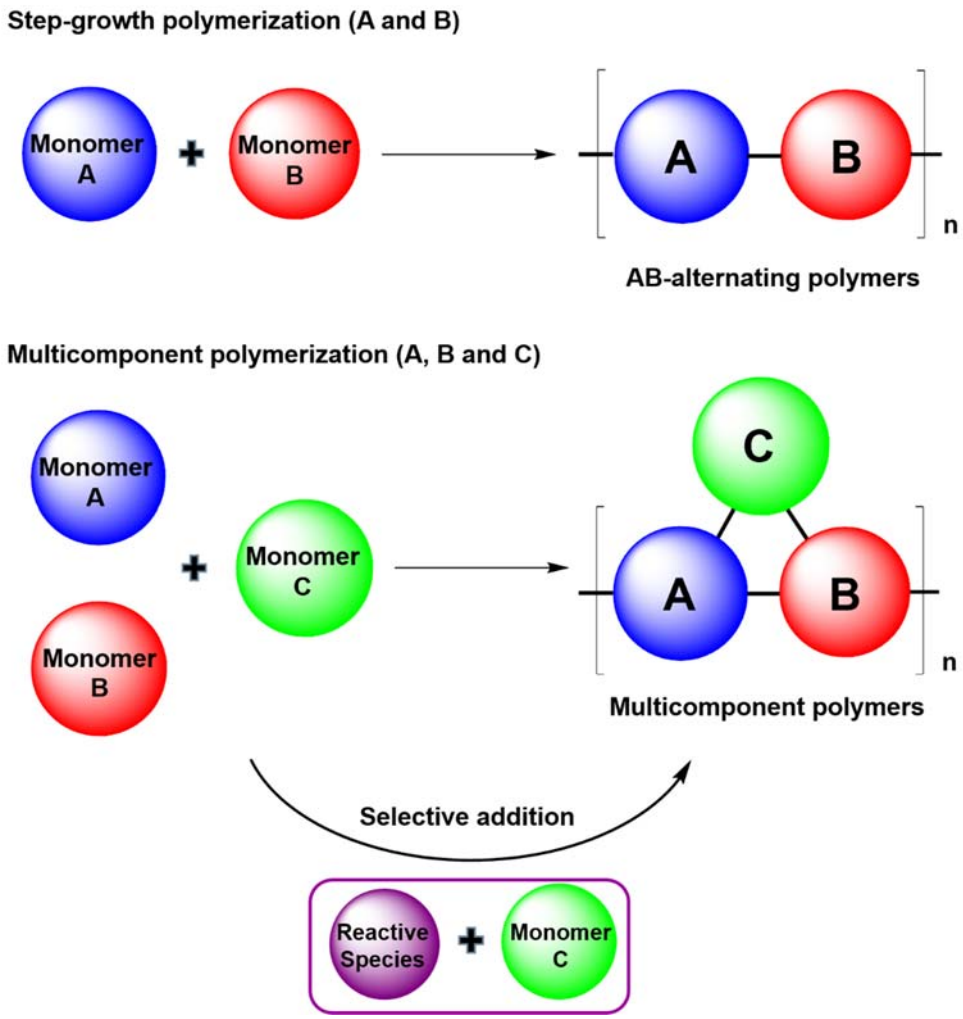


Figure Ⅰ-1. Multicomponent polymerization system

In theory, step polymerization can adopt any organic reactions applying polymerization to AA and BB type monomers. However, not every reaction forms successful polymers due to side reactions and low yield, which cause chain transfer (or defect) and oligomers in step-growth polymerization. This trends are much severe in multicomponent system in the absence of perfect orthogonality among monomers (Figure Ⅰ-1, A, B, and C).

Despite the challenge of multicomponent polymerization, new successful protocol has been welcomed because it can offer efficient and economical manipulation of complex structure of various polymer. Several group reported multicomponent polymers by using representative multicomponent reactions, however, it has limitations of generating oligomers and narrow examples of substrate scope. Overcoming these previous drawbacks, this work describes successful multicomponent polymerization with perfect orthogonality and selectivity that leads well-defined structures and high-molecular weight polymers having extremely broad substrate scope.

2. General Multicomponent Polymerization

Multicomponent polymerization (MCP) constructed by multicomponent reaction is a highly efficient process for making diverse polymers by orthogonal manner. Various reactions such as Cu-catalyzed three-component reaction,[1] Passerini reaction,[2] Mannich reaction,[3] and A^3 coupling[4] have been applied to synthesize many different polymers.[5]

Generally, the multicomponent polymerization uses three or more types of monomers (A, B, and C), whereas typical step-growth polymerization uses two types of monomers (A and B). As a result, a huge number of distinct polymers can be produced by every different combination of monomers.

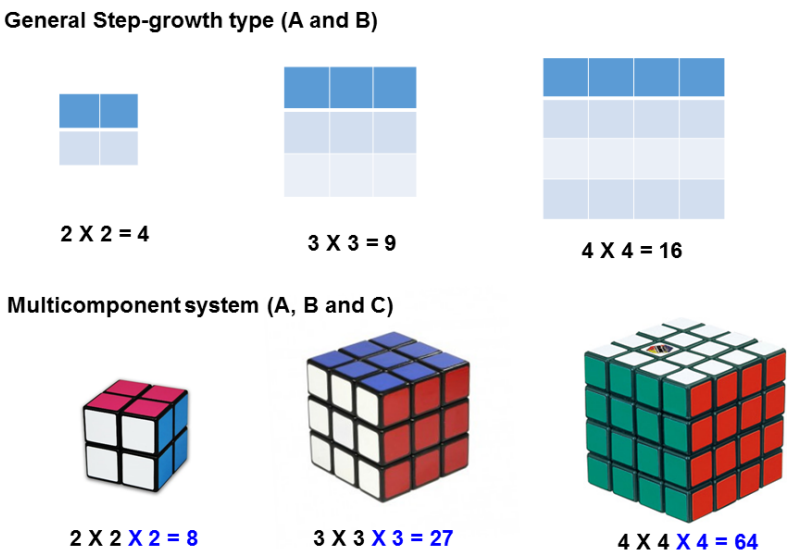
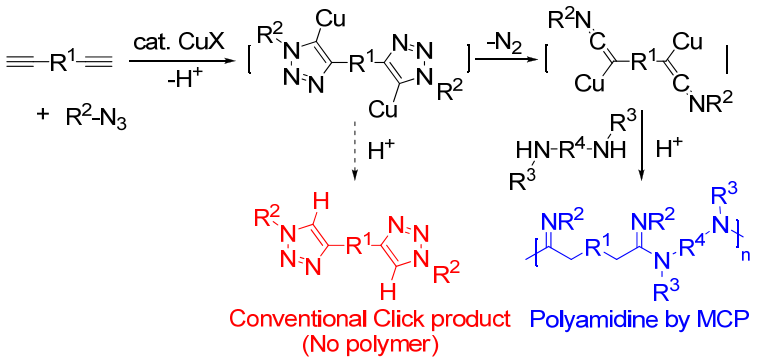


Figure Ⅰ-2. Combination of multicomponent polymerization

Through this process, many polymers having structure such as polyester,[6] poly(ester amide),[7] polyether,[8] poly(ester ether ketone),[9] polyurethane,[10] polythiourethane,[11] and poly(p-phenylenevinylene)[12] were synthesized by MCP based on a step-growth mechanism. However, those polymer systems showed narrow substrate scope and low-molecular weight polymers due to side reactions and low conversions.

3. Cu-Catalyzed Multicomponent Polymerization



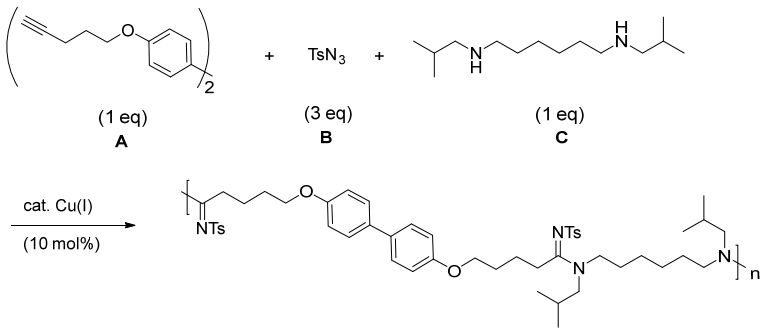
Scheme I-1. Mechanism of Cu-Catalyzed Multicomponent polymerization

Cu-catalyzed multicomponent reaction is extremely selective and efficient reaction based on Click reaction, having broad functional group tolerance. Overcoming general drawbacks of multicomponent system, Cu-catalyzed multicomponent reaction was chosen. This reaction occurs via Cu-catalyzed azide-alkyne cycloaddition

(CuAAC) followed by ring-opening of electron-deficient triazole ring, forming electrophilic keteneimine species. As keteneimine generates, nucleophilic attack of amine forms desired *N*-sulfonylamidine structures. Since we used monomers with bifunctional group, these process makes polyamidines by step-growth mechanism.

Before expanding monomer scope, we tested model reaction with biphenyl spaced diyne (A), tosyl azide (B), and *N,N*-diisobutyl hexyldiamine (C). At initial trial we found out optimized condition for reported monomer reaction was not suitable for polymerization. (Table Ⅰ-1, entry 1) After several attempts to enhance the coupling efficiency of polymer like different Cu(I) salts, the key factor for achieving high conversion was using excess amount of tertiary amine additive (5 eq). Before reaching 5 equivalent of tertiary amine, gradual increase of the amount of additive was tested, however, less than 3 eq of tertiary amine produced similar conversion. Higher molecular weight was observed when adding 3 equivalent but this amount was not suitable for perfect reproducibility. Among different tertiary amine additive, TEA was the best additive for Cu-catalyzed MCP, moreover, 3 equivalent of tertiary amine was not suitable for reproducibility of molecular weight.

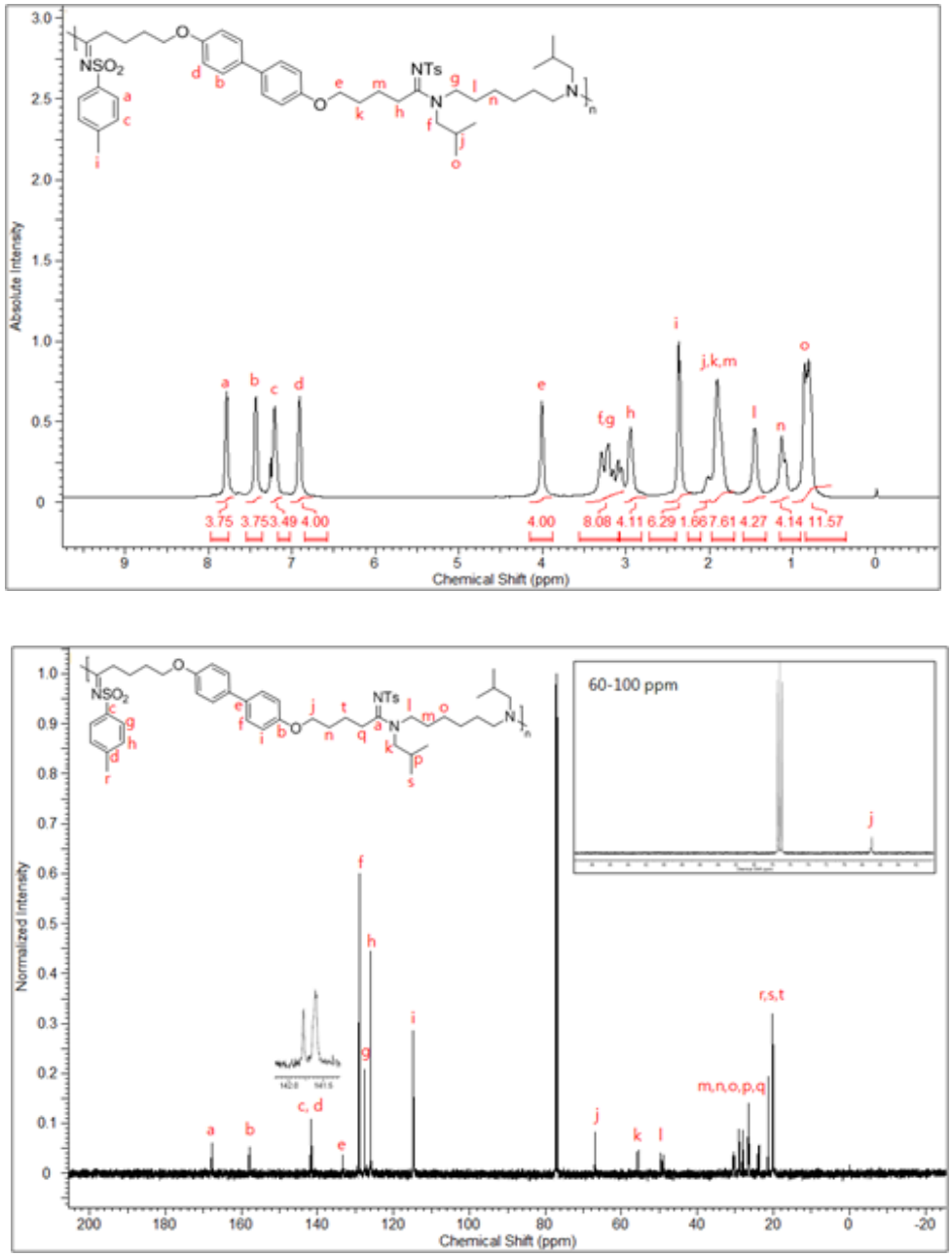
Table Ⅰ-1. Optimization of poly(*N*-sulfonylamindines) Model polymer



entry	catalyst	solvent	conc (M)	temp (°C)	additive (eq)	M_n (PDI)[a]
1	CuI	THF	0.5	50	None	2.7k (1.22)
2	CuI	$CHCl_3$	0.5	50	None	-[b]
3	CuI	DCE	0.5	65	None	2.7k (1.19)
4	CuI	1,4-dioxane	0.5	65	None	2.9k (1.24)
5	CuI	DMF	0.5	70	None	6.2k (1.71)
6	CuBr	DMF	0.5	70	None	7.0k (1.80)
7	$CuBrSMe_2$	DMF	0.5	70	None	6.8k (1.82)
8	$CuBr(PPh_3)_3$	DMF	0.5	70	None	4.9k (1.67)
9	CuCl	DMF	0.5	70	None	7.5k (1.92)
10	CuCl	DMF	1.0	70	TBTA (0.1)	7.3k (1.73)
11	CuCl	DMF	1.0	70	DIPEA (1)	7.4k (1.99)
12	CuCl	DMF	1.0	70	DIPEA (5)	9.7k (3.33)
13	CuCl	DMF	1.0	70	2,6-lutidine (5)	10.3k (2.26)
14	CuCl	DMF	1.0	70	TEA (5)	10.8k (2.81)

[a] Determined by THF SEC calibrated by polystyrene standards. [b] Insoluble in the reaction solution.

Figure Ⅰ-3. ^{1}H and ^{13}C spectra for the model polymer



No signal was detected in 8-9 ppm for ^{1}H NMR spectrum (no Click reaction) and in 60-100 ppm for ^{13}C NMR spectrum except for signals of chloroform and **j** (no Glaser Coupling)

Table Ⅰ-2. Synthesis of Various Poly(*N*-sulfonylamidines)

entry	diyne	sulfonyl azide	diamine	M_n[a] (MALLS)[b]	PDI[a]	yield[c]
1	1a	2a	3a	4.7k (22.4k)	1.52	72%
2	1b	2a	3a	4.8k (23.4k)	1.54	98%
3	1c	2a	3a	6.2k (22.8k)	1.50	79%
4	1d	2a	3a	16.7k (56.1k)	2.99	84%
5	1e	2a	3a	18.2k (63.9k)	2.53	78%
6	1f	2a	3a	10.8k (30.8k)	2.81	76%
7	1f	2b	3a	11.1k (21.5k)	2.16	74%
8	1f	2c	3a	14.6k (–)[d]	3.51	90%
9	1f	2d	3a	16.8k (–)[d]	5.07	85%
10	1f	2e	3a	15.3k (–)[d]	5.92	90%
11	1f	2f	3a	12.2k (20.1k)	1.85	87%
12	1f	2g	3a	10.7k (25.7k)	1.51	93%
13	1f	2h	3a	23.5k (–)[d]	1.77	91%
14	1f	2i	3a	13.2k (44.7k)	1.69	78%
15	1f	2j	3a	7.4k (34.6k)	2.77	66%
16	1f	2a	3b	13.3k (19.9k)	2.97	74%
17	1f	2i	3b	9.7k (43.6k)	1.93	72%
18	1f	2i	3c	8.9k (67.2k)	2.03	79%
19	1f	2i	3d	19.2k (–)[d]	1.97	93%
20	1c	2i	3e	14.5k (31.7k)	1.75	79%
21	1f	2i	3e	12.7k (44.0k)	2.10	77%
22	1f	2i	3f	18.6k (75.1k)	1.91	72%
23	1f	2i	3g	15.7k (–)[d]	2.37	76%
24	1c	2i	3h	8.3k (50.9k)	1.73	71%
25	1f	2i	3h	15.7k (74.9k)	1.53	72%
26	1g	2k	3h	15.0k (–)[d]	1.99	86%

[a] Determined by DMF SEC calibrated by poly(methyl methacrylate) standards (entries 5, 7–14, 16–19, 21–23, 25–26). Determined by THF SEC calibrated by polystyrene standards (entries 1–4, 6, 15, 20, 24). [b] Absolute molecular weight was determined by THF SEC ($CHCl_3$ SEC for entries 11 and 12) using an MALLS detector. [c] Isolated yield after precipitation from selected solvents. [d] Absolute molecular weight could not be obtained because polymers were not soluble in THF and $CHCl_3$

From the analysis of structure of model polymer, well-defined desired polymer structure was observed without Glaser coupling. (Figure Ⅰ-3) Expanding monomer scope also successful regardless of electronic effect of monomers. It should be noted that rigid monomer spacer was helpful for achieving high molecular weight polymers, preventing cyclization process during polymerization.

As a result, various defect-free poly(*N*-sulfonylamidines) were synthesized by Cu-catalyzed MCP. (Table Ⅰ-2) Conversion of the polymerization reaction was significantly enhanced by the excess of base (5 equiv of TEA) with a polar solvent (DMF), while cyclic contaminants were reduced by incorporating long or rigid moieties into the diyne or diamine monomers.

Cu-catalyzed MCP allowed efficient synthesis of highly diverse high-molecular-weight polyamidines from an electronically and sterically wide range of diynes, sulfonyl azides, and diamines, Furthermore, this MCP overcomes the general drawbacks of other MCPs, such as low conversion and narrow substrate scope.

Chapter Ⅱ

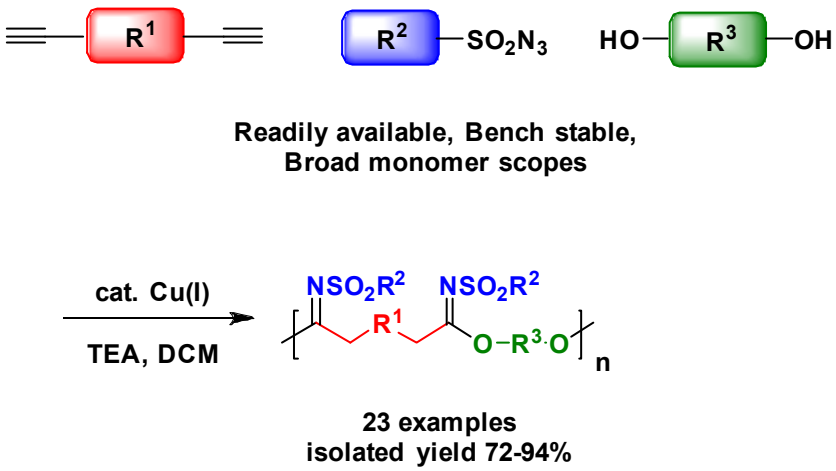
Cu-Catalyzed Multicomponent Polymerization : Preparation of a Library of Poly(*N*-sulfonylimidates)

1. Introduction

Cu-Catalyzed multicomponent polymerization is excellent process for making complex polymer structures with orthogonality among monomers. One of the challenging structure is imidate polymers because of the difficulty of formation of imidate bond and limited substrate scope by using highly unstable monomers. Moreover, polyimidates have particular heat resistance[1] and use in resin materials.[2] In addition, the Chapman rearrangement of polyimidates has produced novel polyamides.[3-5]

However, only rare examples of polyimidate synthesis have been reported because of challenging formation of imidate.[6] Most of the synthesis remained two-component step-growth polymerizations using diols and moisture-sensitive imidoyl chlorides.

Therefore, a new synthetic method for preparing various polyimidates from stable monomers is highly welcomed. If MCP is possible to synthesis of this polymers, preparation problem will be solved, producing various functional imidate polymers. Here, we describe a successful method for the synthesis of various poly(*N*-sulfonylimidates) using Cu-catalyzed multicomponent polymerization (MCP).



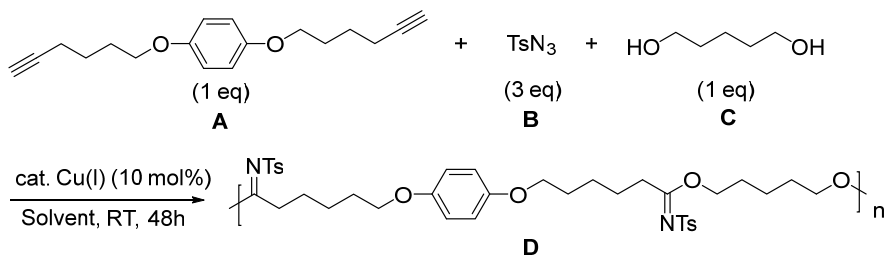
Scheme Ⅱ-1. Synthetic scheme of polyimidates by Cu-Catalyzed multicomponent polymerization

We found that imidate bond can be generated by diol insertion during Cu-catalyzed MCP. Since nucleophilic addition of diamine to electron deficient keteneimine intermediate to construct polyamindine was successful, diol is promising candidate. In this work, different type of diols allowed a library of various polyimidates. Cu-catalyzed MCP using diol produced 23 examples with moderate to high yield of polymer.

Alternative nucleophile, diol, not only solves previous arguing issues but also simply changes access to prepare functional polymers. Furthermore, addition of stable monomer species makes Cu-catalyzed MCP more versatile.

2. Results and Discussion

Table Ⅱ-1. MCP optimization for a model polymer D



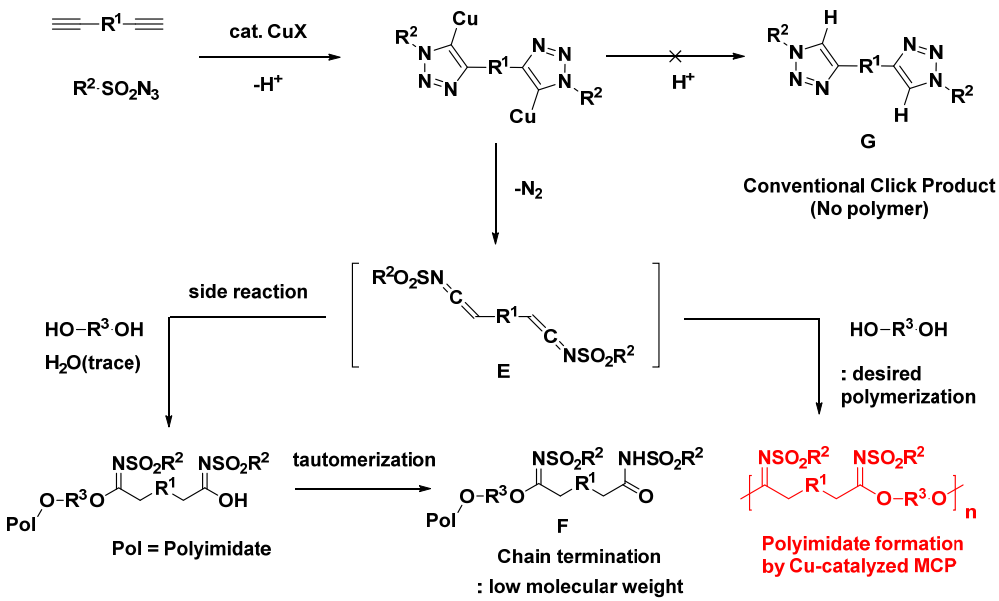
Entry	Catalyst	Solvent	Base	Temp (°C)	Additive (eq)	M_w (PDI)[a]
1	CuCl	DMF	TEA	70	None	6.2k (1.48)
2	CuCl	DMSO	TEA	70	None	5.9k (1.52)
3	CuI	$CHCl_3$	TEA	RT	None	12.8k (2.35)
4	**CuCl**	**DCM**	**TEA**	**RT**	**None**	**16.6k (2.37)**
5	CuCl	DCM	TEA	40	None	8.5k (1.48)
6	CuCl	DCM	TEA	RT	TBTA (0.1)	6.5k (1.58)

[a] Determined by THF size exclusion chromatography (SEC) calibrated by polystyrene standards.

To test the synthesis of polyimidates by MCP, we firstly tested monomers consisted with A, B, and C (Table Ⅱ-1). The previously optimized conditions for the Cu-catalyzed MCP of polyamidines[7] was applied because the new nucleophiles, diols, show excellent nucleophilicity and solubility in *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Although polyamidines works

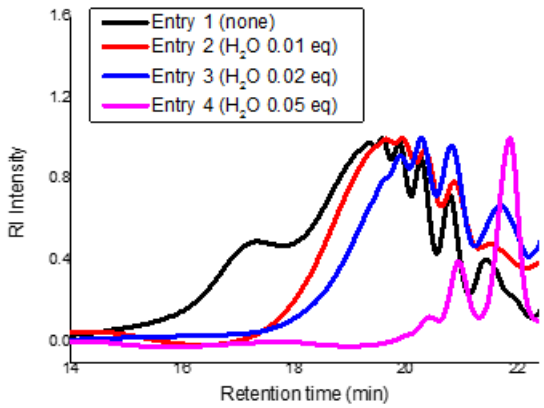
well in this condition, the weight-average molecular weight (M_w) of the resulting poly(*N*-sulfonylimidate) D was very low (Table Ⅱ-1, entries 1 and 2).

Scheme Ⅱ-2. Cu-catalyzed multicomponent polymerization and various pathways leading to side reactions



We suspected that hydroxide from trace amounts of water in these hygroscopic polar aprotic solvents would compete with the bi-functional monomer, diol C. Moreover, once water added to the electrophilic keteneimine E, a key intermediate, it would terminate the polycondensation by forming *N*-sulfonyl amide F through tautomerization (Scheme Ⅱ-2 and Table Ⅱ-2).[1d] For this reason, we concluded that hygroscopic solvent such as DMF and DMSO were not suitable for proper polyimidate synthesis by MCP.

Table Ⅱ-2. SEC traces of Water contamination in model reaction



Entry	Base	Additive (eq)	M_w[a]	PDI[a]
1	TEA (5)	none	16.6k	2.37
2	TEA (5)	H_2O (0.01)	9.2k	1.43
3	TEA (5)	H_2O (0.02)	6.8k	1.39
4	TEA (5)	H_2O (0.05)	2.5k	1.21

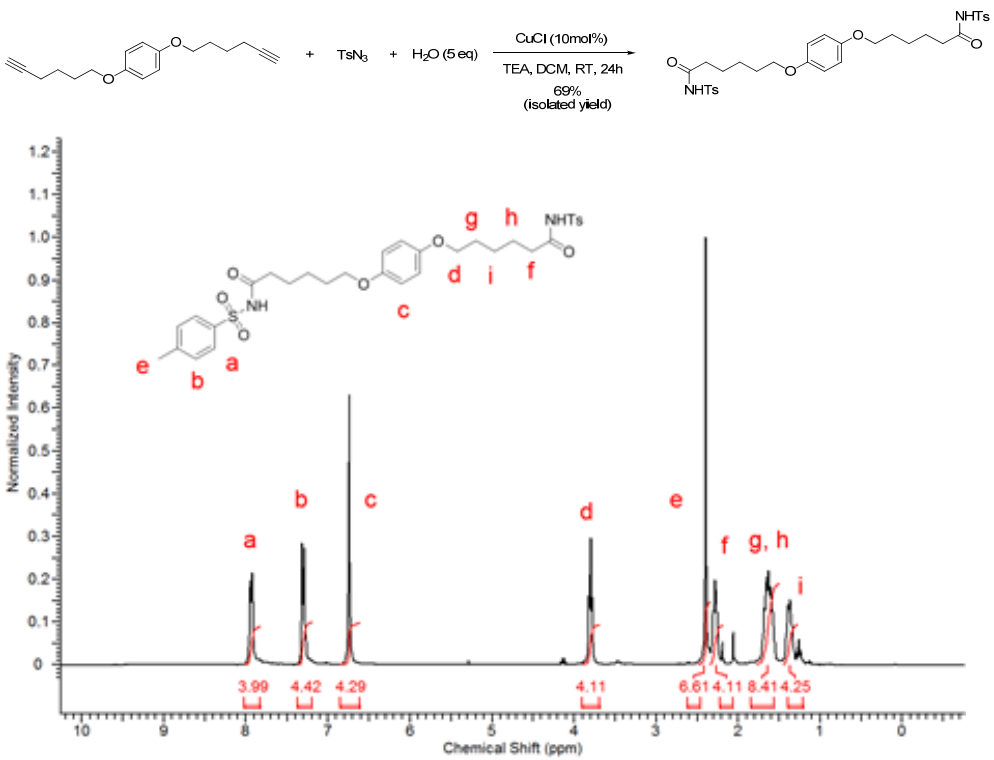
[a] Determined by THF SEC calibrated using polystyrene standards.

To ensure negative effect of water termination, we checked additional water effect. (Table Ⅱ-2) Compare to minimized condition (Table Ⅱ-2, entry 1), molecular weight of polymer significantly dropped from 16.6k to 9.2k to 6.8k, and finally 2.5k when small amount of water (1 mol%, 2 mol %, and 5 mol%, respectively) was added.

Moreover, sulfonyl amide formation by tautomerization also confirmed, as water participated solely nucleophile in basic condition with standard diyne monomer. We observed this final product of water MCP by ^{1}H NMR and MALDI-TOF, respectively. (Figure Ⅱ-1)

Figure Ⅱ-1. Model test of side reaction (^{1}H NMR and MALDI-TOF)

A) ^{1}H NMR spectrum



B) MALDI-TOF

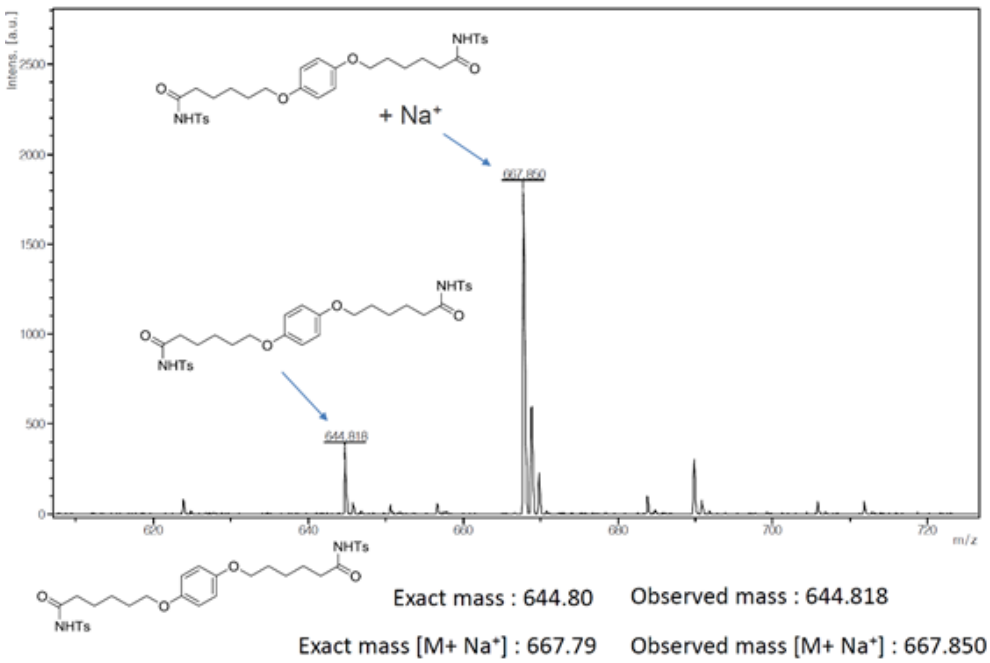
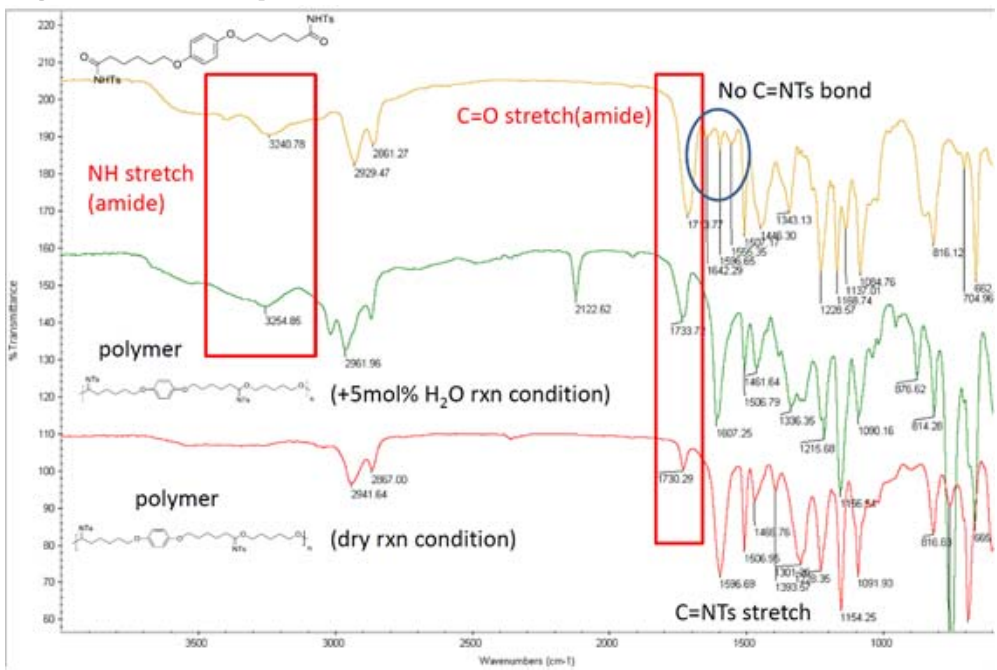


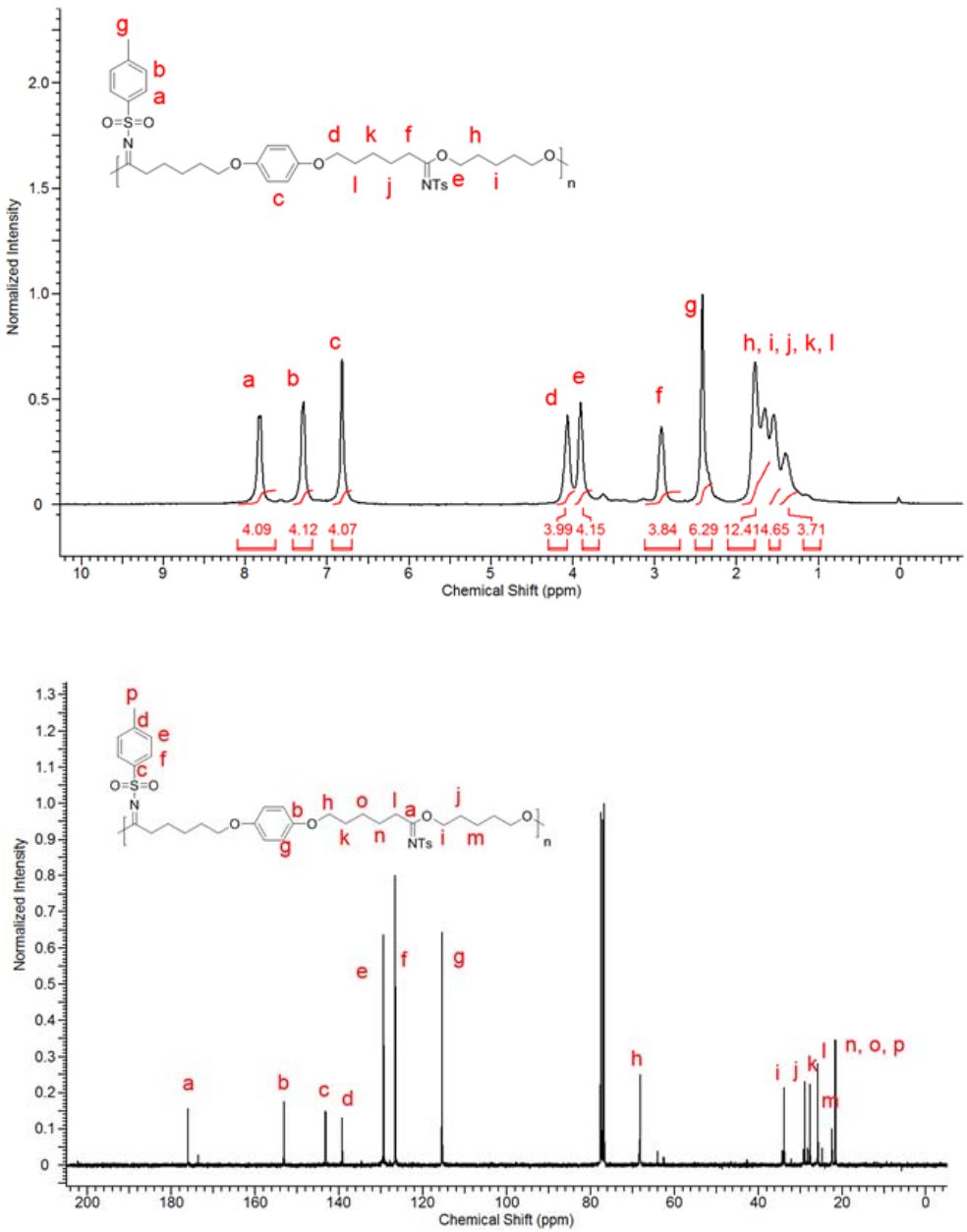
Figure Ⅱ-2. IR spectra of water contamination



With sulfonyl amide compound, we track the formation of sulfonyl amide functional group during polymerization, either. Intrinsic NH stretching comparing pure sulfonyl amide compound appeared in analyzing IR spectrum of wet solvent system of diol MCP. But imine stretching existed in polymer because polymer contains desired imidate functional group as well as sulfonyl amide group. However, extreme dry condition provides disappearance of NH stretching in IR spectrum. (Figure Ⅱ-2)

From these results, minimizing water in the polymerization is important to achieve high conversion in step growth polymerization. Therefore, dry solvents were crucial for polyimidate synthesis and correlated with fact that chlorinated solvents, such as chloroform and dichloromethane (DCM), was the best solvents. Several Cu(I) sources were applied to increase the conversion and among them polymerization using 10 mol% CuCl in DCM at room temperature showed the best result (Table Ⅱ-1, entry 4). Finally, triethylamine (TEA) was found to be the best base for polymerization, and additives such as tris(benzyltriazolylmethyl)amine (TBTA), a ligand known to accelerate CuAAC, gave poor conversion. [7, 8a] (Table Ⅱ-1, entry 6). The conventional click product G, formed by another side reaction that terminates polymerization (Scheme Ⅱ-2), was not observed by analyzing ^{1}H and ^{13}C NMR spectra. (Figure Ⅱ-3) This implied that the Cu-catalyzed MCP was successful and highly selective ring-opening reaction toward triazole formation to form the reactive keteneimine E.[8a, c]

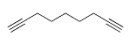
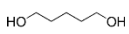
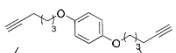
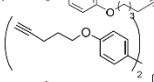
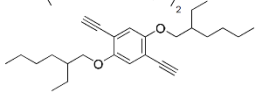
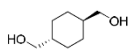
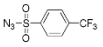
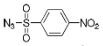
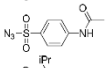
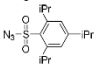
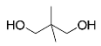
Figure Ⅱ-3. ^{1}H NMR and ^{13}C NMR spectra of the model polymer D

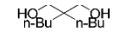
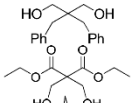
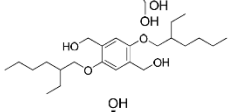
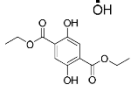
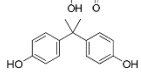


No signal was detected in 8-9 ppm for ^{1}H NMR spectrum (no Click reaction) and in 70-75 ppm for 13C NMR spectrum except for signals of chloroform and h (no Glaser Coupling).

With this optimized conditions in diol MCP, different types of diynes, sulfonyl azides, and diols were examined to broaden the polymerization scope. Although nucleophilicity of diols is weaker than diamines, we synthesized various polyimidates with M_w over 10k, and these results are summarized in Table Ⅱ-3. In general, rigid diynes or diols produced polyimidates with higher molecular weight than when diols with flexible linkers, presumably because of the prevention of intramolecular cyclizations, which leads blocking active end-group of polymerization.

Table Ⅱ-3. Synthesis of various poly(*N*-sulfonylimidates)

Entry	Diyne	Sulfonyl azide	Diol	M_w[a]	PDI[a]	Yield[b]
1	1a	 2a 	3a 	11.2k	1.93	89%
2	1b		2a	3a	16.6k	2.37	82%
3	1c		2a	3a	17.4k	1.83	87%
4	1d		2a	3a	9.5k	2.02	76%
5	1b	2a	3b 	12.8k	2.08	90%
6	1b	2b 	3b	10.7k	2.36	84%
7	1b	2c 	3b	10.5k	1.55	80%
8	1b	2d 	3b	13.8k	1.73	93%
9	1b	2e 	3b	33.5k	1.52	90%
10	1b	2f 	3b	20.2k	2.02	92%
11	1a	2f	3b	26.3k	2.66	94%
12	1e	2f	3b	32.2k	2.98	87%
13	1b	2f	3c 	15.1k	1.64	72%

14	1b	2f	3d		28.9k	2.33	91%
15	1b	2f	3e		19.7k	1.97	83%
16	1b	2f	3f		17.6k	1.73	82%
17	1b	2f	3g		19.4k	2.23	87%
18	1c	2f	3h		11.6k	1.52	81%
19	1e	2f	3h		17.3k	1.53	89%
20	1b	2a	3i		10.9k	1.73	74%
21	1b	2f	3j		13.3k	1.85	88%
22	1a	2f	3k		12.7k	2.02	91%
23	1b	2f	3k		16.5k	2.01	93%
24	1e	2f	3k		16.3k	2.30	90%

[a] Determined by THF SEC calibrated using polystyrene standards (entries 1–7, 14, 15, 18-24). Determined by DMF SEC calibrated using poly(methyl methacrylate) standards (entries 8 and 9). Determined by $CHCl_3$ SEC calibrated using polystyrene standards (entries 10-13, 16, 17).[b] Isolated yield after precipitation into selected solvents.

Polymerization with various diyne was explored and initially achieved with commercially available sources such as 1,8−nonadiyne, p−toluenesulfonyl azide and 1,5−pentanediol, yielding moderate M_w (Table Ⅱ−3, entry 1). Introducing more rigid phenyl or biphenyl groups on diyne monomers made polymers with higher M_w (Table Ⅱ−3, entries 2 and 3). However, MCP of highly rigid and reactive aromatic diyne (1d) gave relatively low−molecular weight polymer, presumably because of the less stability of diyne, causing decomposition during the reaction. This brings a stoichiometric imbalance of polymerization resulting in lower conversion (Table Ⅱ−3, entry 4).

Next, we examined different types of sulfonyl azides for MCP containing an electron withdrawing group [CF_3 (2c), NO_2 (2d)] and

electron donating group [NHCOMe (2e), 2,4,6-tris-iPr (2f)] (Table Ⅱ-3, entries 7-10). Regardless of the electronic nature of the arylsulfonyl azide, various polyimidates having moderate to high M_w up to 33.5k were obtained. Nucleophilic addition of the diol works well in the use of the sterically hindered sulfonyl azide (2f), and the aliphatic azide (2b) was also found to be a proper monomer for MCP (Table Ⅱ-3, entries 6 and 10).

Finally, we tested diol family to achieve expansion of the monomer scope. Monomers having primary alcohols were found to be good substrates for MCP (Table Ⅱ-3, entries 13-16). Also, monomers containing cyclic (3b), bicyclic (3g) and aromatic diols (3h) were applicable to MCP (Table Ⅱ-3, entries 10, 17 and 18). In addition, although it has been reported that the imidate product afforded in moderate yield due to its steric hindrance [1b], secondary diol (3i) was suitable monomer for MCP (Table Ⅱ-3, entry 20).

Moreover, MCP showed excellent functional group tolerance, affording well-defined structures in the presence of ester and alkene functionalities. Interestingly, bisphenol type monomers successfully formed desired polymer structures, despite their weaker nucleophilicity (Table Ⅱ-3, entries 21-24). Commercially available bisphenol A (3k) polymerized as well with different combination of monomers. Although it was previously reported that the yield of Cu-catalyzed multicomponent reactions in small molecule synthesis was only 61%,1b our optimized conditions for MCP of phenolic monomers (3j and 3k) showed efficient nucleophilic addition to keteneimines, affording a M_w up to 16.5k.

Table Ⅱ-4. Thermal analysis of various poly(*N*-sulfonylimidates)

entry[a]	T_d(°C)	T_g(°C)	T_m(°C)	entry[a]	T_d(°C)	T_g(°C)	T_m(°C)
1	233	-	-	13	302	44	-
2	286	-	-	14	208	39	-
3	293	26	-	15	217	51	-
4	270	-	-	16	278	-	58
5	292	28	-	17	285	63	-
6	286	25	-	18	262	53	-
7	272	29	-	19	257	81	-
8	225	12	-	20	302	-	-
9	307	77	-	21	190	36	-
10	298	55	-	22	274	62	-
11	281	65	-	23	291	49	-
12	274	68	-	24	287	-	-

[a] Entry of Table 2. 10 wt% decomposition temperature (T_d), glass transition temperature(T_g), and melting temperature(T_m) of various poly(*N*-sulfonylimidates)

The successful polymerization of phenol monomers suggested that the rigidity of phenolic nucleophiles may play a positive role in polymerization. However, since diols are much weaker nucleophiles than diamines, the MCP to prepare polyimidates is inevitably limited by even a small amount of water contamination, and this results in a lower conversion in the synthesis of polyimidates compared with polyamidines.[12] Additionally, the longer reaction time is another downside of this MCP. Still, the decomposition temperature of resulting polyimidates obtained by thermal gravimetric analysis

was ranging from 190 °C to 307 °C, which showed good stability at high temperature (Table Ⅱ-4).

3. Conclusion

In summary, we synthesized a library of poly(N-sulfonylimidates) with moderate to high molecular weights via the Cu-catalyzed MCP of diynes, sulfonyl azides, and diols. Because of the mild conditions, we were able to pre-pare twenty-three different poly(*N*-sulfonylimidates) from readily available and bench stable monomers (five diynes, six sulfonyl azides, and ten diols). Minimizing water con-tamination was key to achieving the successful MCP of poly(*N*-sulfonylimidates).

Chapter Ⅲ

One-Shot Synthesis of Graft and Dendronized Polymerization

1. Introduction

Graft and dendronized polymers have linear polymers or dendrons as their side chains, having distinguished composition of main chain. These side chains repel each other by severe steric hindrances, leading that the polymer main chains to have enthalpically favored extended conformation. It makes these polymers act as worm-like structures or cylindrical nano-objects.[1] Their one dimensional structure produces hundreds of nanometer-long macromolecules covered with bulky side chains, which opens up numerous potential applications in nanoscale electronics[2] or biomaterials.[3] However, constructing precisely defined microstructures of these complex macromolecules for utilizing them as high-performance materials remains a challenge because 'noble' orthogonality should be prepared during the synthesis of polymer ensuring that there are no interferes between formation of main chains and bulky side chains. Especially, finding the right reactions to overcome steric congestion of repeat units and bulky side chains to produce high-molecular-weight polymers with high selectivity is a demanding task.

2. Background

Three synthetic methods typically are used for preparing graft and dendronized polymers: 'graft-to', 'graft-from' and 'graft-through'. The 'graft-to' method[4] requires preformed main chains having connecting site to introduce the final side chains, either long polymer chains or large dendrons. (Figure Ⅲ-1a). Click chemistry is widely used for this approach, where side chains are

attached directly to the polymer backbone.[5] However, steric hindrance interferes perfect grafting of bulky side chains so that defects can be formed.

The more popular method is the second : the 'graft-from' method (Figure Ⅲ-1b).[6] This needs preformed backbone as well but the difference is that small monomers were added on to main chains to make bulky side chains. The backbone contains initiating site so that the side chains can be grown by [e.g. atom transfer radical polymerization (ATRP)] or by coupling small dendrons one by one. Because organic molecules can easily penetrate among the large side chains or dendrons and be perfectly removed by purification step, higher grafting densities and pure final products are the main advantage of this method. However, some defects still can arise from incomplete coupling, causing chain transfer or cross-linking, which results in broad dispersity in the side chains. Moreover, this process requires multiple steps in real and a significant amount of time.

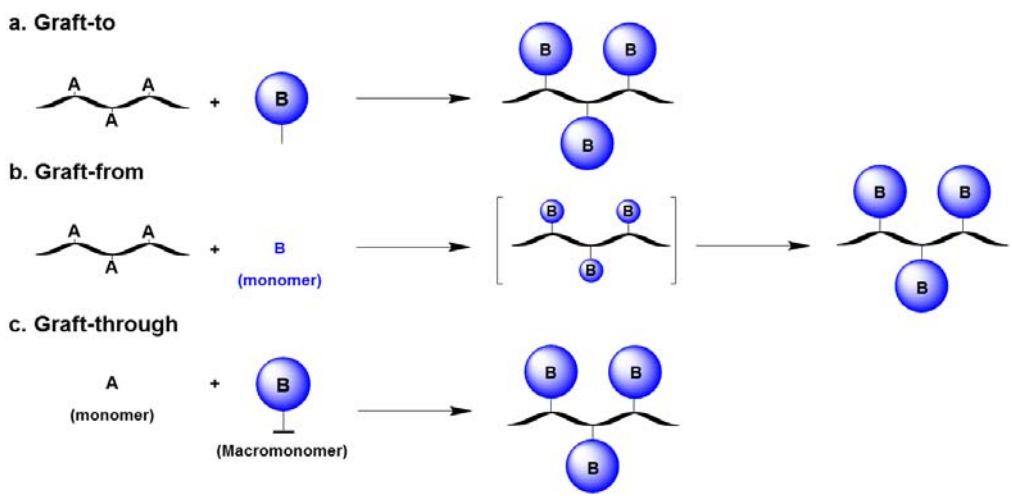


Figure Ⅲ-1. Traditional method for Graft polymers

The final method is the ‘graft-through’ or ‘macromonomer approach’ (Figure Ⅲ-1c) [7] In this method, monomers containing the final linear polymers or dendrons undergo polymerization such as ATRP,[8] reversible addition-fragmentation chain-transfer polymerization (RAFT),[9] ring-opening metathesis polymerization (ROMP),[10] or polycon-densation.[11] Although this approach allows for the preparation of perfect polymer architecture, overcoming steric hindrance of large volume of macromonomer is still biggest challenge to produce high-molecular-weight polymers. All three methods commonly takes long reaction times, multistep synthetic sequences, and repeated purification for removing large excess amounts of monomers. As a result, preparing well-defined complex polymers or a library based on diversity-oriented polymerization has been particularly challenging because of the difficulties of such a drawbacks and the narrow substrate scope.

Part A. Graft Polymerization

3. Results and Discussion

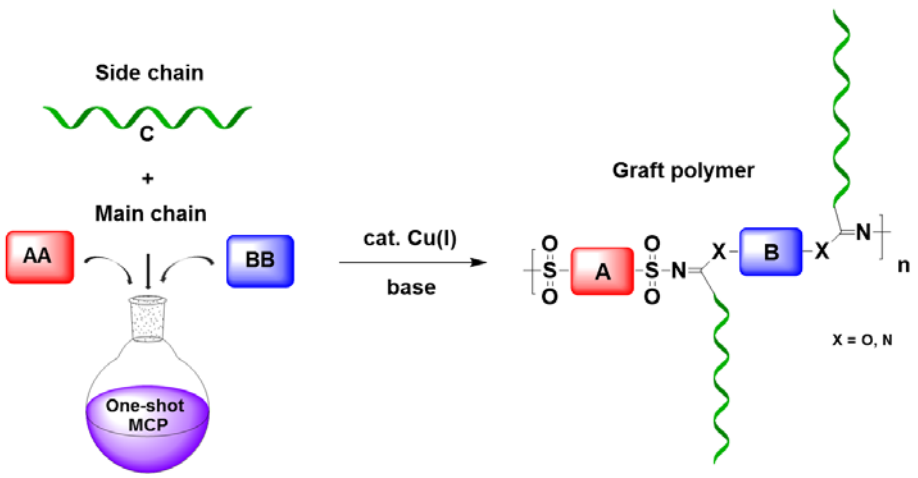
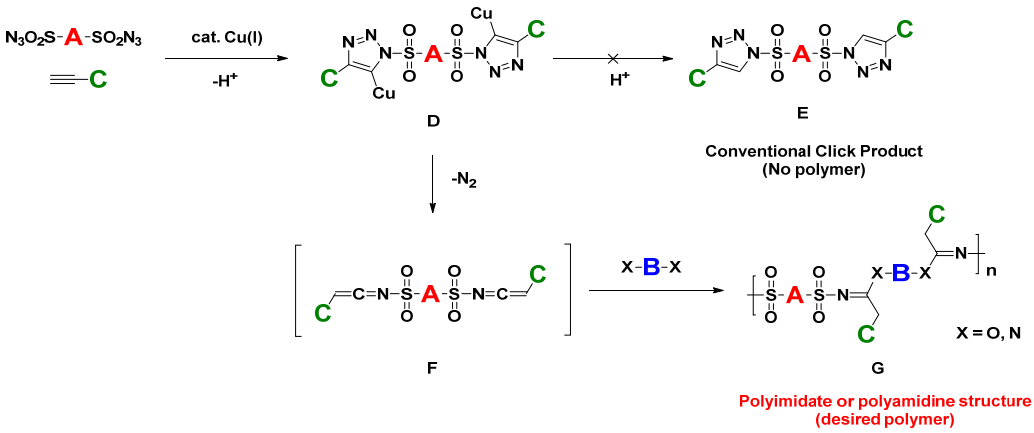


Figure Ⅲ-2. One-shot Graft Polymerization by Cu-catalyzed MCP

To address this issue, we applied multicomponent polymerization (MCP) to provide highly diverse polymer structures prepared from three or more monomers (A, B and C).[12-18] Also, powerful MCP allows providing an efficient and step-economical route for synthesizing graft and dendronized architectures with simultaneous adjustment of polymer main chains and side chains in a one-shot reaction. But the most remaining challenge is to overcome the severe sterics between repeat side chains that can produce high-molecular- weight polymers.



Scheme Ⅲ-1. Mechanism of One-shot Graft and Dendronized Polymerization by Cu-catalyzed MCP

For attempt to examine the polymerization, we used bis-sulfonyl azides, diamines (or diols) as AA- and BB-type monomers for the construction of the main backbone, while a macromonomer (C) formed side chains of polymer structures with containing various dendrons or linear polymers terminated by easily accessible alkyne functional groups. Various mono-functionalized macromonomers were easily prepared by simple protocol.

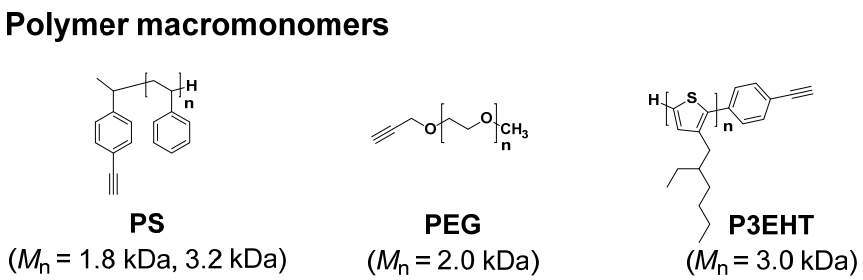
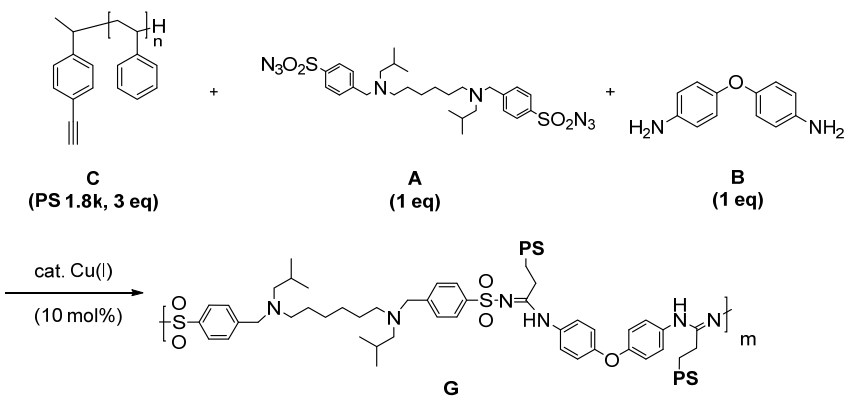


Figure Ⅲ-3. Mono-functionalized polymer macromonomers

Polymer macromonomers such as Polystyrene (PS), terminated by alkyne, was prepared by ATRP using an initiator containing silyl-protected alkyne[22] and poly(3-(2′-ethyl)hexylthiophene) (P3EHT) was prepared by Grignard metathesis (GRIM) polymerization, followed by Stille coupling of phenylacetylene moiety.[23] In addition, commercially available polyethylene glycol (PEG) was used for synthesizing mono-functional PEG from simple alkylation with alkyne group.

Table Ⅲ-1. MCP Optimization for a Model Polymer



Entry	Catalyst	Solvent	Base	Temp	M_n (MALLS)[a]	PDI[a]	DP[b]
1	CuCl	DMF	TEA	70	42.0k	1.39	9.6
2	CuCl	DMF	TEA	110	84.9k	1.44	19
3	CuCl	DMF	TEA	110[c]	38.0k	1.17	8.7
4	$Cu(ACN)_4PF_6$	DMF	TEA	110	87.8k	1.43	20
5	**$Cu(ACN)_4PF_6$**	**Tol/DMF**	**TOA**	**110**	**122.1k**	**2.03**	**28**

[a] Absolute molecular weights (g/mol) determined by THF size-exclusion chromatography (SEC) using MALLS detector. [b] Degree of polymerization was determined by absolute molecular weight (MALLS) divided by MW of repeat unit. c Sealed tube condition.

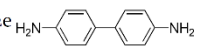
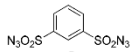
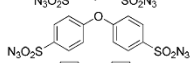
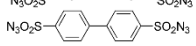
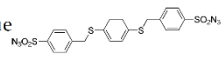
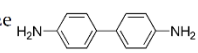
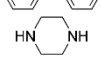
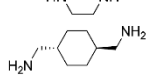
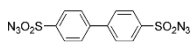
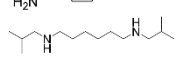
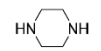
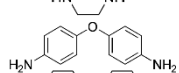
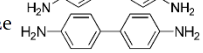
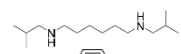
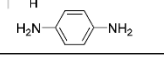
At first, we tested MCP using bis-sulfonyl azide (A), diamine (B), and a

polystyrene macromonomer (C, M_n = 1.8 kDa) for the model study. The initial attempt used the same conditions (CuCl, DMF at 70° C) optimized in our previous multicomponent polymerization reported on the synthesis of poly(*N*–sulfonylamidines). [19] However, the reaction mixture became very viscous as polymerization undergoes but finally stuck, leading the results with low conversion. By analyzing the multi angle laser light scattering (MALLS) detection, a graft polymer yieldied with M_n = 42.0 kDa, which translates to a degree of polymerization (DP) of 9.6. (Table Ⅲ-1, entry 1)

To increase conversion of the polymerization, the reaction temperature was elevated to 110° C, above the glass transition temperature (T_g) of PS to improve the stirring condition. The DP was thus increased to 19. (Table Ⅲ-1, entry 2) On the other hand, the same condition with a sealed tube lowered the DP (or the conversion of the polymerization) because nitrogen evolution, one of the driving forces, was suppressed (Table Ⅲ-1, entry 3). Next, we examined other Cu(I) sources to increase the conversion, and found that $Cu(ACN)_4PF_6$ containing non-nucleophilic bulky counteranions showed slightly better results under the same conditions (Table Ⅲ-1, entry 4). Finally, tri-*n*-octyl amine (TOA) instead of TEA increased conversion showing highest DP of 28 (Table Ⅲ-1, entry 5), presumably by lowering the viscosity of total reaction mixture as a plasticizer effect.

Table Ⅲ-2. Synthesis of Various Graft Polymers

Entry	Macromonomer	Bis-sulfonyl azide	Diamine	M_n[a] (MALLS)[b]	PDI[a]	DP[c]	α[d]	Yield
	PS (1.8k)			1.80k	1.04	18.0		
1	PS	1a	2a	15.5k (113.4k)	1.56	25.7	0.90	77%
2	PS	1a	2b	22.0k (76.8k)	2.37	17.9	0.95	82%
3	PS	1a	2c	22.2k (122.1k)	2.46	27.9	0.88	78%

4	PS	1a		2d		24.7k (123.8k)	1.63	29.4	0.94	86%
5	PS	1a		2e		18.2k (463.4k)	3.01	111.1	1.13	88%
6	PS	1b		2e		14.8k (223.4k)	2.15	54.8	0.78	69%
7	PS	1c		2e		15.8k (140.4k)	3.31	34.0	0.90	75%
8	PS	1d		2e		18.7k (113.6k)	2.43	27.6	1.09	74%
9	PS	1e		2e		20.0k (357.8k)	3.17	83.6	0.67	70%
	PS (3.2k)					3.20k	1.08	32.0		
10	PS	1a		2e		51.1k (347.3k)	3.03	48.4	1.18	78%
11	PS	1a		2f		30.4k (148.3k)	1.57	21.0	1.01	75%
12	PS	1a		2g		28.9k (183.0k)	1.35	25.7	1.01	71%
13	PEG (2.0k)	1d		2a		8.5k (75.2k)	1.20	16.5	0.85	86%
14	PEG (2.0k)	1d		2f		10.9k (49.8k)	1.20	11.3	0.89	82%
15	PEG (2.0k)	1d		2c		11.0k (111.8k)	1.24	24.7	0.86	85%
16	PEG (2.0k)	1d		2e		10.3k (270.1k)	1.32	59.8	0.88	88%
17	P3EHT (3.0k)	1a		2a		27.8k (112.0k)	1.64	16.4	0.74	70%
18	P3EHT (3.0k)	1a		2b		21.6k (124.4k)	2.10	18.6	0.80	72%

[a] Determined by THF size exclusion chromatography (SEC) calibrated by polystyrene standards. [b] Absolute molecular weight was determined by THF size-exclusion chromatography (SEC) using MALLS detector. (Table 2, entries 1-4, 10-18) Absolute molecular weight was determined by chloroform SEC using MALLS detector. (Table 2, entries 5-9) [b] Degree of polymerization was determined by absolute molecular weight (MALLS) divided by MW of repeat unit. [c] Shape parameter obtained by Mark-Houwink-Sakurada plots from SEC-viscometry analysis.

With the optimized conditions, we expanded the monomer scope by applying various combinations of bis-sulfonyl azides, diamines, and macromonomers for the synthesis of graft polymers. Since Cu-catalyzed MCP revealed the highly efficiency and selective performance, we prepared a library of 18 graft polymers with high molecular weights and high yields, as summarized in Table Ⅲ-2. The shape parameter (α) from Mark-Houwink-Sakurada plots from SEC-viscometry analysis produced the information of behavior of these graft polymers in solution state. One can estimate how different combinations of

monomers affected the α values. (for a sphere, $\alpha = 0$; for a random coil, $\alpha < 0.8$; for a rod-like structure, $0.8 < \alpha < 2.0$; for a perfect rod, $\alpha = 2.0$)

We initially explored various diamines as nucleophiles and prepared various high-molecular-weight graft polymers having 1.8k PS as a side chain. The DP range of graft polymers was 18–111 calculated from absolute molecular weight by analysis of MALLS data (Table Ⅲ-2, entries 1–5). Both flexible alkyl diamines (2a) and aromatic diamines (2b–2d) produced graft polymers having similar DP values (Table Ⅲ-2, entries 2–4), whereas rigid and more nucleophilic benzidine (2e) produced a graft polymer with the highest DP value of 111 (Table Ⅲ-2, entry 5).

There was a trend that the shape parameter (α) seemed to increase as polymer backbone became flat and stiff by using linear-shaped diamines instead of flexible or bent ones (Table Ⅲ-2, entries 1 and 3 vs. entry 5). Also, MCP using various bis-sulfonyl azides (1b–1e) and benzidine (2e) resulted successful graft polymers with DPs of 28–84 (Table Ⅲ-2, entries 6–9). Again, use of a more rigid and linear monomer combination seemed to induce polymer with higher rigidity (Table Ⅲ-2, entry 8).

Next, we examined MCP using almost double PS side chains (M_n = 3.2 kDa) as macromonomers and combined rigid benzidine (2e) as a nucleophile. A high-molecular-weight graft polymer having a DP of 48 was produced (Table Ⅲ-2, entry 10). Also, nucleophilic piperazine (2f) and primary amine (2g) successfully produced high-molecular-weight graft polymers with DPs of 21 and 26, respectively (Table Ⅲ-2, entries 11 and 12)

Furthermore, we tested MCP for other macromonomers with different polymer structures. Commercially available and widely used PEG (M_n = 2.0 kDa) was also a good macromonomer. Rigid biphenyl sulfonyl azide (1d) in combination

with flexible diamine (2a) or piperazine (2f) afforded moderate-molecular-weight graft polymers with DPs of 17 and 11, respectively (Table Ⅲ-2, entries 13 and 14, respectively). On the other hand, changing nucleophiles to rigid aryl diamines (2c and 2e) produced higher-molecular-weight polymers with DPs of 25 and 60, respectively (Table Ⅲ-2, entries 15 and 16, respectively). These graft polymers containing flexible PEG side chains showed α values higher than 0.8, implying that they adopted an extended conformation in solution (Table Ⅲ-2, entries 13-16).

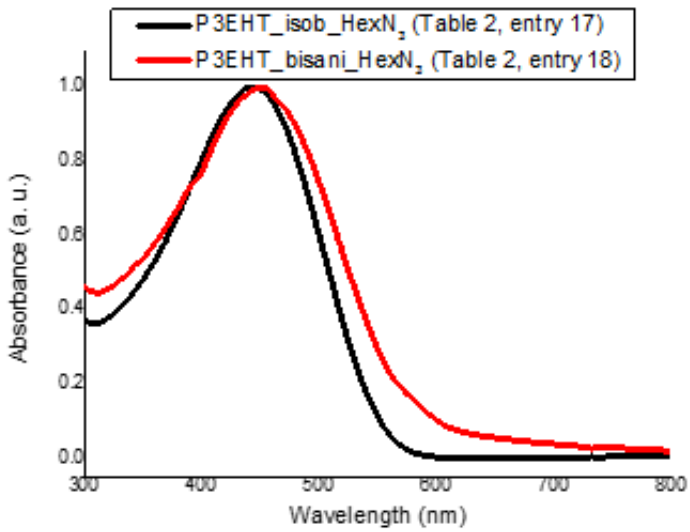


Figure Ⅲ-4. UV-Vis spectra of P3EHT graft polymers

Finally, the semiconducting side chains, conjugated polymer P3EHT (M_n = 3.0 kDa), was a promising macromonomer as well, providing moderate molecular weights with DPs of 16 and 19 (Table Ⅲ-2 entries 17 and 18, respectively). From UV-vis analysis, these polymers showed maximum absorption at 443 nm and 451 nm, respectively, in the film state with an optical band gap of 2.18 eV (Figure Ⅲ-4). Throughout the preparation of graft polymers, glassy and non-polar

polystyrene, polar PEO, and even semiconducting P3EHT successfully constructed various graft polymers based on diversity-oriented synthesis. All of polymers was easily prepared by the one-shot Cu-catalyzed MCP method.

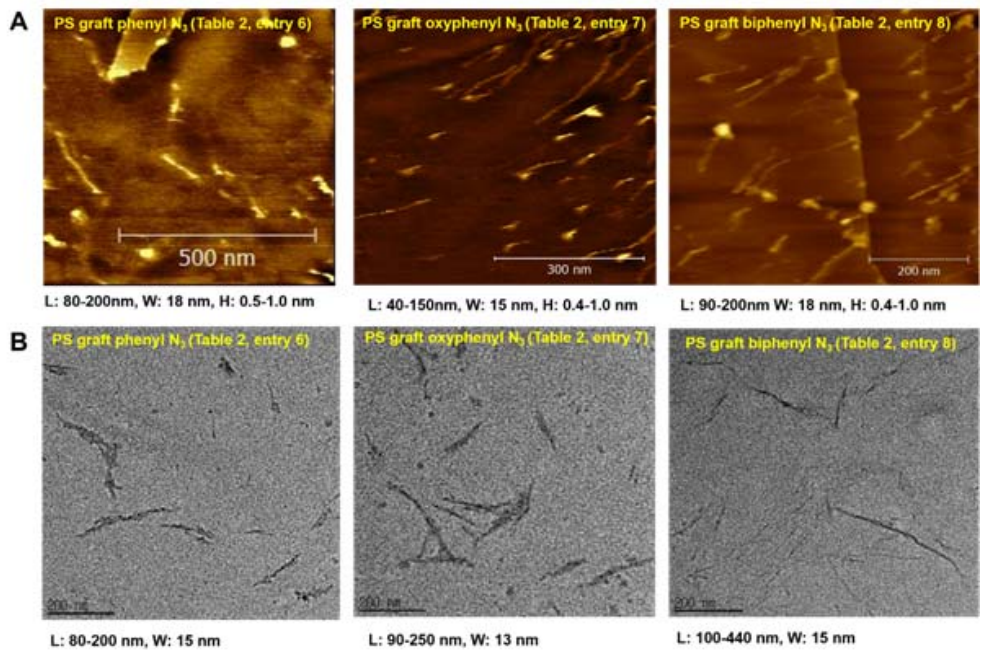


Figure Ⅲ-5. AFM (A) and TEM (B) Images of Graft Polymers

We investigated more about the conformation of these graft polymers by checking direct visualization of the products, although the shape parameter, α, already suggested that would adopt extended chain conformation. The graft polymers were visualized by atomic force microscopy (AFM) and transmission electron microscopy (TEM) because of the large size of these complex macromolecules. Particularly, monomer combinations of rigid aryl diamine (2b and 2e) and aryl bis-sulfonyl azides (1b-1d) produced electron-rich aryl backbones, which allowed direct imaging by TEM without any staining (Figure Ⅲ-5). Indeed, single chains of graft polymers prepared from PS, benzidine (2e), and aryl bis-sulfonyl azides (1b, 1c, and 1d) showed extended conformation by AFM and TEM.

From AFM imaging on a highly oriented pyrolytic graphite (HOPG) surface, the observed single chains showed lengths of 200 nm, widths of 15–18 nm, and heights of 0.5–1.0 nm. Because of the low height, getting high-resolution images by AFM was exceptionally challenging. However, TEM revealed better images with higher contrast showing similar lengths from 100 to 200 nm and widths of 13–15 nm (Figure Ⅲ-5).

Table Ⅲ-3. Thermal analysis of various graft polymers

Entry[a]	T_d(°C)	T_g(°C)	T_m(°C)	Entry[a]	T_d(°C)	T_g(°C)	T_m(°C)
1	331	82	-	10	346	101	-
2	364	89	-	11	396	101	-
3	337	88	-	12	353	102	-
4	325	77	-	13	360	-	51
5	372	91	-	14	382	-	55
6	348	90	-	15	372	-	55
7	348	93	-	16	368	-	52
8	328	89	-	17	442	-	-
9	328	96	-	18	409	-	-

10 wt% decomposition temperature (T_d),glass transition temperature(T_g), and melting temperature(T_m) of various graft polymers– [a] Table III-2

Lastly, all these resulting graft polymers showed great thermal stability. The T_d of graft polymers ranged from 325 to 442 ° C. All the graft polymers except the PEGlated polyamidines [Table Ⅲ-3, entries 13–16; melting temperature (T_m) = 52–55 ° C] were

shown to be amorphous without any melting transition as determined by differential scanning calorimetry (DSC).

Part B. Dendronized Polymerization

4. Results and Discussion

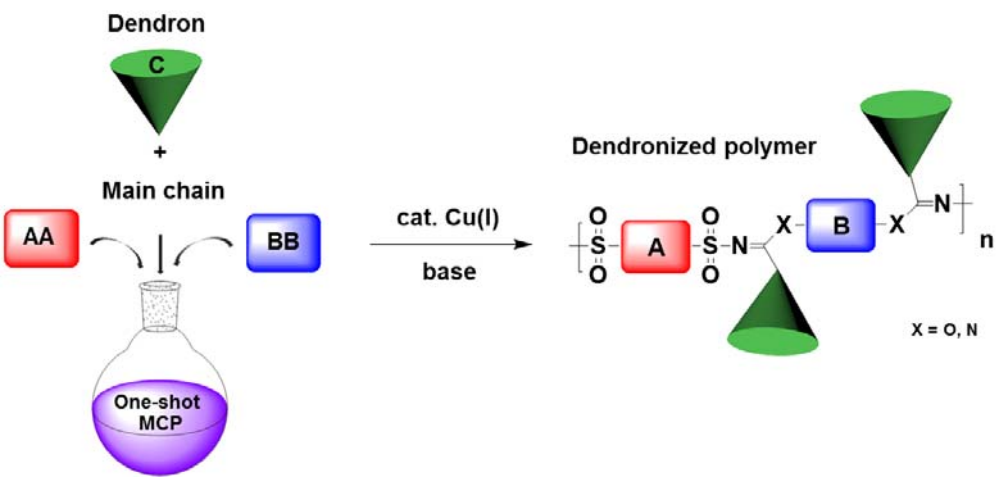


Figure Ⅲ-6. One-shot Synthesis of Dendronized Polymers by Cu-catalyzed MCP

With the successful preparation of graft polymers by Cu-catalyzed MCP, we examined the synthesis of dendronized polymers as well. We chose five different types of dendrons containing alkynes (Fréchet,[24] Müllen,[25] ether,[26] ester,[27] and thiophene types[28]) with two different sizes for the generation for each dendron. These 10 dendronized macromonomers have molecular weights ranged from 500 Da to 2.4 kDa (Figure Ⅲ-6).

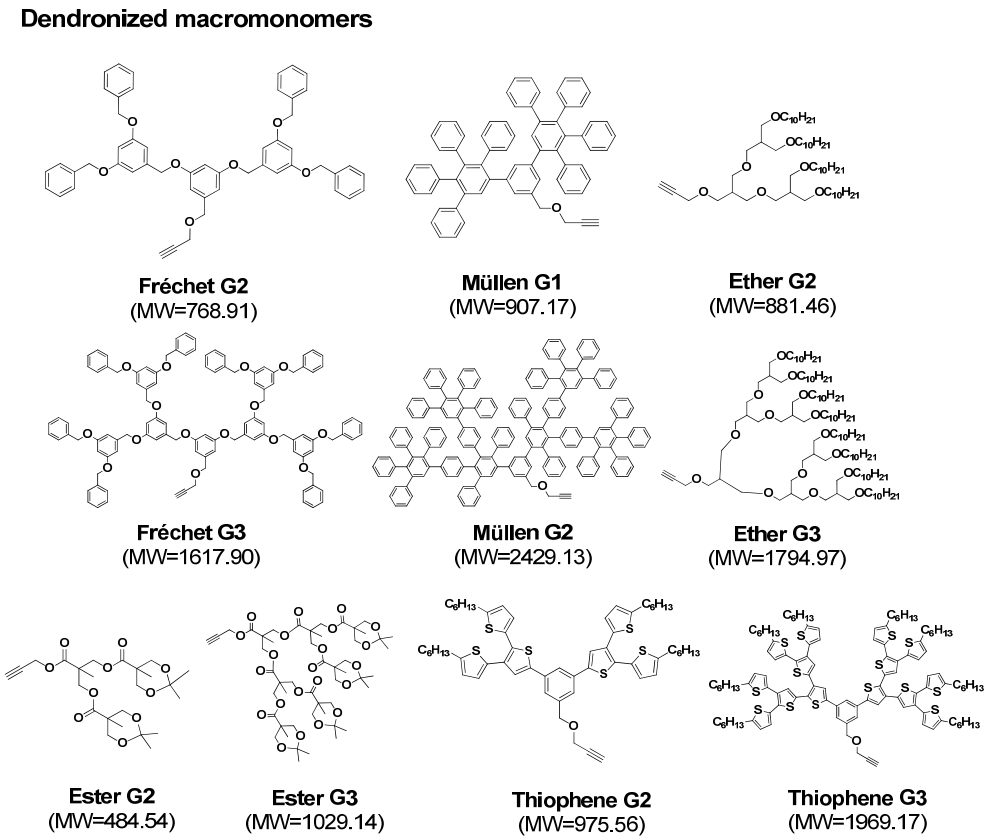
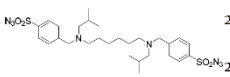
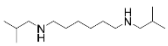
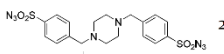
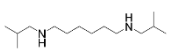
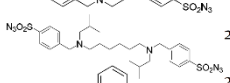
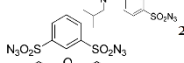
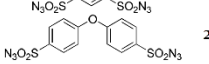
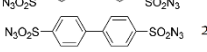
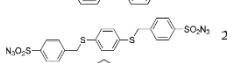
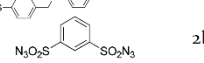
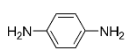
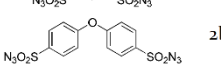
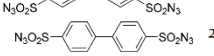
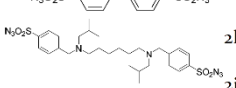
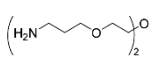
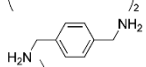
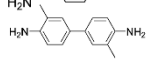
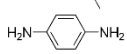
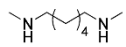
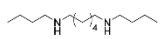
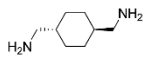
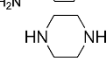
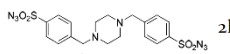
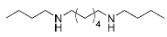
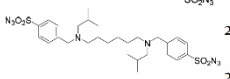
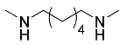
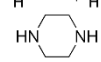


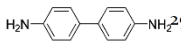
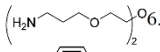
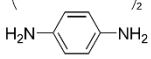
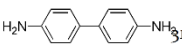
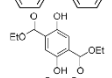
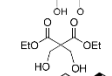
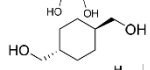
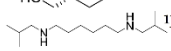
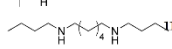
Figure Ⅲ-7. Various types of Mono-functionalized dendrons

After successful preparation of these dendron macromonomers, we extended this MCP method to the synthesis of dendronized polymers. Dendrons are a special type of macromolecules that has perfectly defined branching and show high solubility and low viscosity. Thus, this leads the fact that there was no viscosity problem or less as graft polymer synthesis during polymerization. Now, in the synthesis of dendronized polymers, more readily accessible TEA was used instead of TOA as the optimized reaction condition.

Table Ⅲ-4. Synthesis of Various Dendronized Polymers

Entry	Macromonomer	Bis-sulfonyl azide	Diamine / Diol	M_n[a] (MALLS)[b]	PDI[a]	DP[b]	α[c]	Yield
1	Fréchet G2	1a 	2a 	12.2k (91.3k)	1.35	39	1.06	73%
2	Fréchet G2	1a	2f 	28.6k (572.0k)	1.58	249	1.04	79%
3	Fréchet G3	1f 	2a 	27.0k (209.1k)	1.56	53	1.16	70%
4	Fréchet G3	1a 	2a	18.3k (353.7k)	1.51	87	1.03	71%
5	Fréchet G3	1b 	2a	15.8k (143.3k)	1.44	39	1.14	65%
6	Fréchet G3	1c 	2a	21.2k (364.7k)	1.58	96	1.19	77%
7	Fréchet G3	1d 	2a	14.8k (211.2k)	1.46	56	1.16	81%
8	Fréchet G3	1e 	2a	17.2k (94.0k)	1.32	24	0.94	75%
9	Fréchet G3	1b 	2b 	31.1k (507.5k)	1.87	141	1.19	65%
10	Fréchet G3	1c 	2b	30.6k (301.6k)	3.26	82	0.96	70%
11	Fréchet G3	1d 	2b	19.0k (463.4k)	2.85	125	1.38	73%
12	Fréchet G3	1a 	2h 	19.3k (125.7k)	1.45	32	0.73	66%
13	Fréchet G3	1a	2i 	18.7k (210.5k)	2.05	53	0.81	71%
14	Fréchet G3	1a	2d 	22.3k (782.1k)	1.86	194	1.22	78%
15	Fréchet G3	1a	2b 	31.4k (1041k)	1.62	265	1.06	79%
16	Müllen G1	1a	2j 	12.8k (69.1k)	1.40	27	0.84	71%
17	Müllen G1	1a	2k 	22.4k (184.2k)	1.69	70	0.87	78%
18	Müllen G1	1a	2g 	20.1k (86.9k)	1.36	35	1.03	73%
19	Müllen G1	1a	2f 	31.5k (106.8k)	2.19.	43	0.70	72%
20	Müllen G1	1f 	2k 	14.6k (41.0k)	1.59	16	1.14	81%
21	Müllen G2	1a 	2j 	21.0k (58.4k)	1.40	11	0.96	84%
22	Müllen G2	1a	2f 	22.8k (129.0k)	1.48	24	1.00	82%

First, macromonomer containing popular and easily prepared second-generation Fréchet dendron was tested for MCP. Both flexible diamine (2a) and cyclic diamine (2f) produced high-molecular-weight dendronized polymers with DPs of 39 and 249, respectively (Table Ⅲ-4, entries 1 and 2, respectively).

23	Müllen G2	1a	2e		29.2k (66.9k)	1.52	12	1.10	80%
24	Ether G2	1a	2a		8.4k (51.1k)	2.42	21	0.97	75%
25	Ether G2	1a	2h		6.5k (47.9k)	1.61	18	1.05	70%
26	Ether G2	1a	2b		21.8k (197.2k)	2.60	81	1.07	71%
27	Ether G2	1a	2f		13.5k (53.5k)	1.42	22	1.19	70%
28	Ether G3	1a	2f		16.1k (68.9k)	1.67	16	1.03	82%
29	Ether G3	1a	2e		31.4k (61.8k)	1.60	15	0.94	80%
30	Ester G2	1a	2l		5.1k (57.6k)	1.56	32	0.75	71%
31	Ester G2	1a	2m		5.4k (32.8k)	1.67	19	0.72	72%
32	Ester G3	1a	2n		14.2k (99.8k)	2.02	36	1.06	76%
33	Thiophene G2	1a	2a		13.8k (44.7k)	1.42	25	0.85	70%
34	Thiophene G2	1a	2k		11.9k (147.7k)	1.42	54	0.96	71%
35	Thiophene G3	1a	2a		11.3k (125.2k)	1.54	20	0.95	77%
36	Thiophene G3	1a	2k		8.6k (65.7k)	1.42	14	1.03	71%

[a] Determined by THF size exclusion chromatography (SEC) calibrated by polystyrene standards. [b] Absolute molecular weight was determined by THF size-exclusion chromatography (SEC) using an MALLS detector. (Table 3, entries 1-8, 12-36) Absolute molecular weight was determined by chloroform SEC using an MALLS detector. (Table 3, entries 9-11) [b] Degree of polymerization was determined by absolute molecular weight (MALLS) divided by MW of repeat unit. [c] Shape parameter obtained by Mark-Houwink-Sakurada plots from SEC-viscometry analysis.

Expanding to larger macromonomer containing more soluble third-generation Fréchet dendron allowed us to use various combination of bis-sulfonyl azides and diamines, and high-molecular-weight dendronized polymers with DPs ranging from 24 to 265 were obtained (Table Ⅲ-4, entries 3-15). Using rigid and linear monomers, MCP became more efficient presumably due to suppressed cyclization. Especially, as compared to other more flexible diamines, linear aromatic diamines (2b and 2d) produced very high-molecular-weight dendronized polymers with DPs above 100 and higher α values (Table Ⅲ-4, entries 5 vs. 9, 7 vs. 11, 12 vs. 14, and 13 vs. 15).

Next, we examined the possibility of another non-polar Müllen-type dendron as a potential macromonomer. Notably, even first-generation dendron has high molecular weight and high steric bulkiness (Figure Ⅲ-7, MW = 907.17 Da). For this reason, the resulting dendronized polymer showed lower solubility and lower conversion than Fréchet dendrons, producing moderate-molecular-weight polymers with DPs between 16 and 70 (Table Ⅲ-4, entries 16–20). For example, using a more soluble diamine containing longer alkyl chains (2j vs. 2k) might have increased the DP from 27 to 70 (Table Ⅲ-4, entries 16 and 17). By introducing more nucleophilic diamine monomers (2f and 2g), polymers with high DPs of 35 and 43 were obtained (Table Ⅲ-4, entries 18 and 19). On the other hand, rigid bis-sulfonyl azide (1f) might result in lower DPs of dendronized polymers as com-pared to the case of using flexible bis-sulfonyl azide (1a), presumably due to the lower solubility of the polymer (Table Ⅲ-4, entries 17 vs. 20).

On the other hand, attempts to use second-generation Müllen dendron as a macromonomer also produced dendronized polymers successfully, although their DPs were somewhat lower, between 11 and 24 (Table Ⅲ-4, entries 21 and 22), due to their extremely bulky side chains as compared to other dendrons (Figure Ⅲ-7, MW = 2429.13 Da). Still, Cu-catalyzed MCP was efficient enough to produce high-molecular-weight polymers of 58.4–129 kDa by overcoming huge steric hindrance during each coupling reaction. It seemed that those dendronized polymers became more rigid when the size of the dendrons increase. The shape parameter, α, of the dendronized polymers synthesized from the same combination of bis-sulfonyl azide (1a) and diamines (2j and 2f) increased from 0.84 to 0.96 and from 0.70 to 1.00, respectively, when a bigger macromonomer (second-generation Müllen dendron) was attached (Table Ⅲ-4, entries 16 vs. 21 and entries 19 vs. 22, respectively).

More polar alkyl ether dendrons were also suitable macromonomers for MCP when reacted with various diamines. Because both second- and third-generation ether dendrons are liquid, the polymerizations were conducted at neat conditions to enhance the conversion. With the macromonomer containing second-generation alkyl ether dendron, MCP successfully produced high-molecular-weight polymers with DPs of 18 to 81 (Table Ⅲ-4, entries 24-27). Among them, rigid and linear aryl diamine (2b) produced the highest-molecular-weight dendronized polymer presumably due to suppressed intramolecular cyclization (Table Ⅲ-4, entry 26). Attempts to use a larger macromonomer containing third-generation ether dendron, however, produced polymers with lower DPs of 15 or 16 because larger steric congestion and dilution caused by the larger volume of total reaction mixture would inevitably decrease the conversion (Table Ⅲ-4, entries 28 and 29).

We further examined other polar ester dendrons as macromonomers for MCP, but using diamines as nucleophiles failed because they underwent side reactions such as transamidation with ester functionality on the side chains and produced insoluble gels. Thus, we changed to much weaker nucleophiles, diols instead, which showed function-al-group tolerance toward ester functionality. MCP successfully afforded dendronized polymers containing G2 and G3 esters by using the previously optimized conditions in dichloromethane at room temperature (Table Ⅲ-4, entries 30-32).[20] Similar to other cases, larger third-generation dendrons generally showed higher α values (Table Ⅲ-4, entry 32).

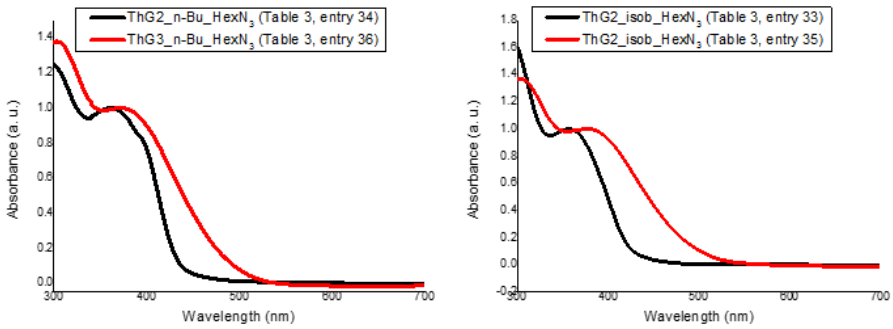


Figure Ⅲ-8. UV-Vis spectra of Thiophene dendronized polymers

Lastly, we tested macromonomers containing thiophene dendrons to show that dendronized polymers containing conjugated side chains could be prepared by MCP as well. Indeed, the MCP produced high-molecular-weight polymers containing second-generation thiophene dendron with DPs of 25 and 54 (Table Ⅲ-4, entries 33 and 34), whereas those containing larger third-generation thiophene dendron showed somewhat lower conversion, with DPs of 20 and 14, similar to other cases (Table Ⅲ-4, entries 35 and 36). These dendronized polymers containing conjugated thiophene side chains showed optical band gaps of 2.85 eV (G2) and 2.53 eV (G3) (Figure Ⅲ-8)

Single chains of dendronized polymers consisting of Fréchet dendrons and aryl-rich main chains from bis-sulfonyl azides (1b, 1c, and 1d) and diamine (2b) also exhibited extended conformation, as shown by AFM and TEM imaging (Table Ⅲ-4, entries 9-11). AFM showed that these polymers had lengths up to 200 nm, heights of 0.3-1.2 nm, and widths of 5-8 nm. Also, a similar range of lengths of 175-210 nm and widths of 6 nm were observed by TEM (Figure Ⅲ-9). The width of dendronized polymers seemed to be lower than that of

graft polymers because the side chains of dendronized polymers were obviously shorter.

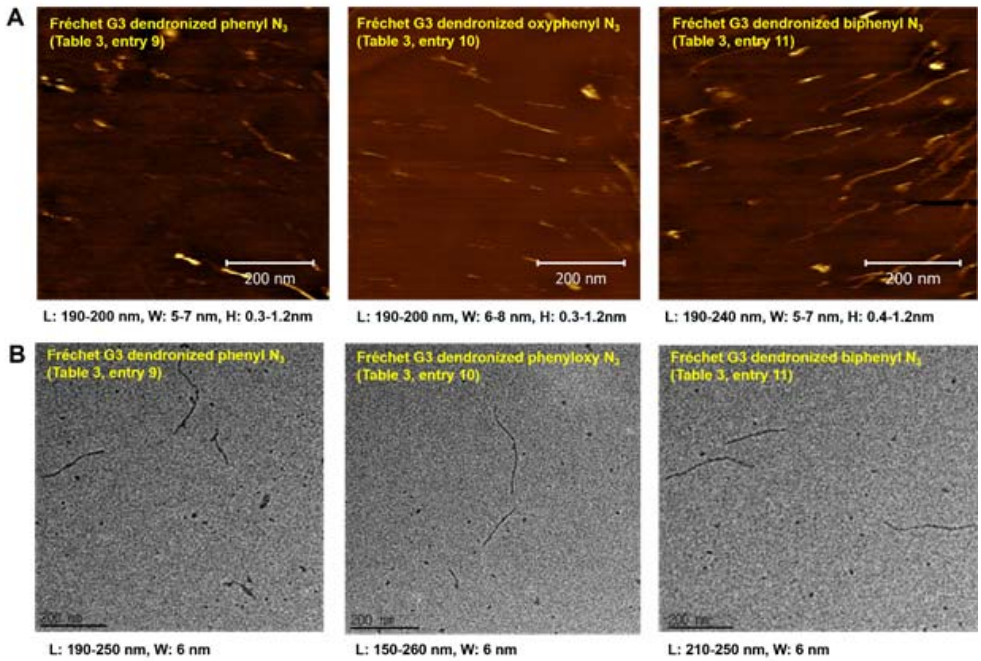


Figure Ⅲ-9. AFM (A) and TEM (B) Images of Dendronized Polymers

A few exceptions were the dendronized polymers containing ester dendrons, whose T_d ranged from 251° C to 260 ° C. It seems that the ester linkages would be less stable at such high temperatures. Finally, most of resulting dendronized polymers showed great thermal stability. The T_d of dendronized polymers ranged from 312 ° C to 419 ° C (Table Ⅲ-5).

Table Ⅲ-5. Thermal analysis of Various dendronized polymers

Entry[a]	T_d(°C)	T_g(°C)	T_m(°C)	Entry[a]	T_d(°C)	T_g(°C)	T_m(°C)
1	354	44	-	19	341	176	-
2	352	47	-	20	355	-	-
3	361	53	-	21	419	-	-
4	357	45	-	22	395	121	-
5	342	52	-	23	408	-	-
6	312	53	-	24	347	-	-
7	359	50	-	25	318	-	-
8	350	53	-	26	326	-	-
9	345	50	-	27	338	-	-
10	353	51	-	28	367	-	-
11	354	50	-	29	353	-	-
12	368	41	-	30	255	-	-
13	361	51	-	31	251	46	-
14	348	54	-	32	260	46	-
15	351	47	-	33	337	-	-
16	333	149	-	34	332	-	-
17	355	-	-	35	325	-	-
18	354	-	-	36	327	-	-

10 wt% decomposition temperature (T_d), glass transition temperature(T_g), and melting temperature(T_m) of various dendronized polymers– [a]Table III-4

5. Conclusion

In summary, we synthesized a library of high-molecular-weight graft and dendronized polymers with good yield by one-shot Cu-catalyzed multicomponent polymerization. Finding optimized conditions, such as using a more active catalyst, enhancing proper solubility, and lowering the viscosity of the reaction mixture, was the key to successful MCP. The biggest advantage of MCP was that the broad monomer scope enabled us to obtain various complex macromolecules by adjusting the compositions of the main chains and side chains simultaneously in one-shot synthesis.

For example, one could tune various properties such as flexibility, polarity, and conjugation of both the main backbone and the side chains. Therefore, diversity-oriented polymerization became possible by extremely efficient and step-economical MCP. However, since this MCP adopts nucleophiles at high temperature, mild condition should be applied to guarantee tolerance of ester group. Plus, electrophilic functional groups such as acyl/alkyl halide are limited to prevent low conversion and chain transfer in one-shot polymerization.

To demonstrate the power of this method, 54 different high-molecular-weight graft and dendronized polymers were prepared from eleven diamines, three diols, six bis-sulfonyl azides, and fourteen macro-monomers containing alkynes (four linear polymers and ten dendrons). Most of the polymers showed rigid conformation with a shape parameter, α, larger than 0.8. Generally speaking, these α values seemed to increase with the incorporation of larger macromonomers, whereas the DP inevitably decreased due to steric congestion. From AFM and TEM imaging, we confirmed the extended conformation of the single chain morphologies.

Chapter Ⅳ

Multi-Graft Polymerization
(Graft-to Strategy)

1. Introduction

Graft polymers has received much attention in polymer chemistry due to its unique microstructure and properties. Compared to simple linear polymer, graft polymers have many applicable field, such as biomedical field, electronics, nanomaterial and absorbents. However, this functional material mostly has been focused its structures limited two major components: structures of backbone and side chain. Therefore, constructing various type of graft polymer is still challenging.

In general, graft polymers can be synthesized by three different approach, 'graft-from', 'graft-to', and 'graft-through' method. Among them, the 'graft-to' method is known to easy approach with simple tethering to main chain, so called post-modification method. This methodology directly introduces side chains or large dendrons to decorate main backbone. However, severe steric congestion between each side chain interrupt each grafting coupling on repeat unit of main chain.

To solve this problem, highly efficient coupling process were welcomed. Click chemistry is one of promising coupling reaction for this approach, where side chains are coupled directly onto the grafting site of the polymer backbone.[1-10] Despite of applying good coupling reaction, the resulting polymers limited in terms of the diversity having only two different factors.

2. Results and Discussion

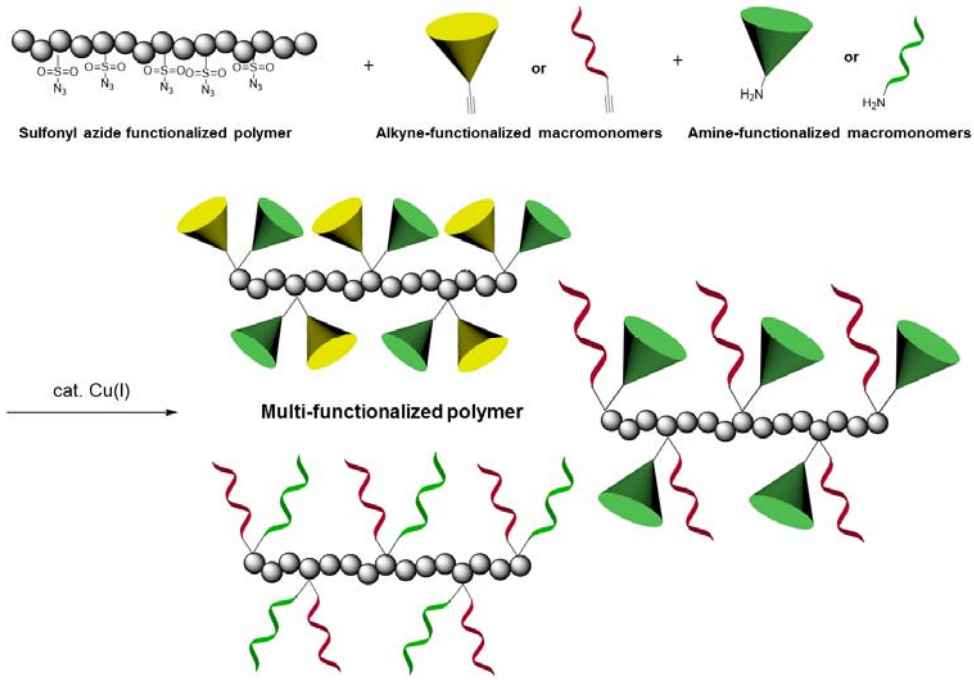


Figure Ⅳ-1. Multi-graft polymerization (graft-to method)

Previously, we construct successful methodology by using Cu-catalyzed multicomponent polymerization, producing successful polymers by graft-through manner. Even though we can apply diversity on polymer, side chains still uniformed single component. However, if we focus on side chains where the functional part located on, converting MCP to 'graft-to' method, diverse side chain or dendrons can be applied to single polymer main chain. Definetly, this will produce multi-graft polymers. (Figure Ⅳ-1) As depicted above, any macromonomers can be tethered to backbone polymer to produce

graft polymers with distinct combinations of side chains.

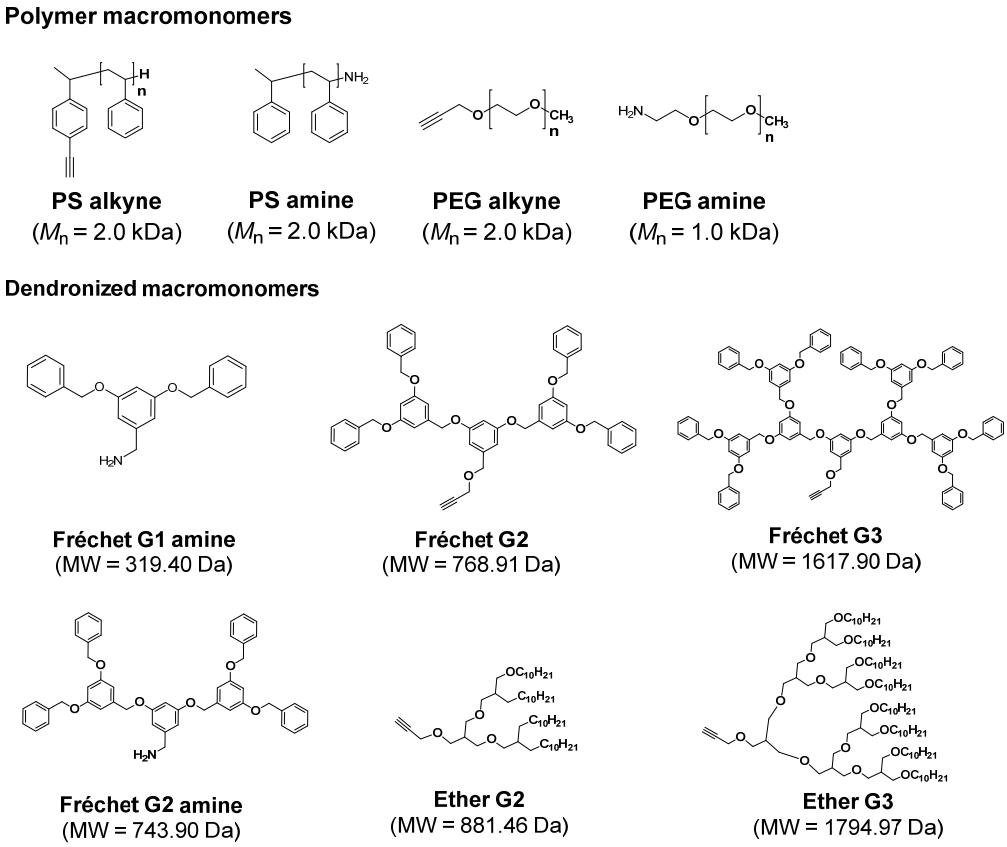
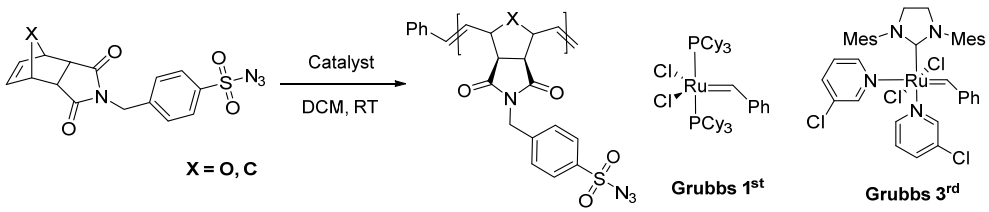


Figure Ⅳ-2. Various Mono-functionalized macromonomers

To synthesize this hierarchical polymer structure, mono-functionalized macromonomers such as alkyne and amine functional group were chosen for easy accessibility of monomers. In theory, one can apply any possible units or macromolecules that ended with those kind of functional group. Moreover, because any kind of bis-substituted monomers can generate gels via chain transfer reaction, monomers having single functional group is crucial for successful

modification. Thus, in this study, we prepared different side chains having distinct mono end-groups (Figure Ⅳ-2)

Table Ⅳ-1. Sulfonyl azide polymer synthesis



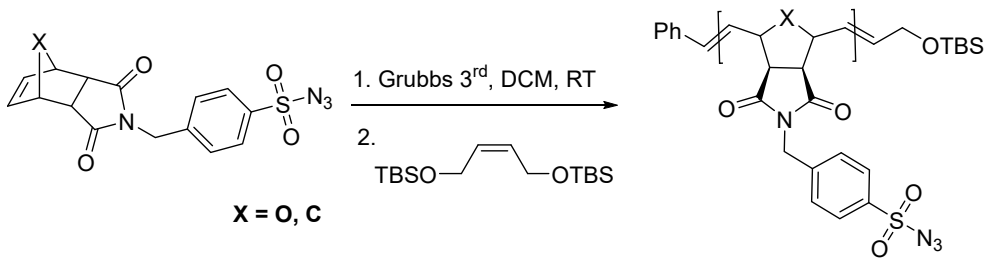
Entry	Monomer	Catalyst	Feeding ratio (M/I)	Conversion	M_n [a]	PDI[a]
1	Oxanorb	Grubbs 1st	30	>99%	8.9k	1.37
2	Oxanorb	Grubbs 3rd	30	>99%	9.1k	1.05
3	Exo-norb	Grubbs 3rd	30	>99%	8.9k	1.06

[a] Determined by THF SEC calibrated using polystyrene standards

We prepared main chain composed of oxanorbornene or norbornene. To ensure efficient coupling of macromonomers toward main backbone, 100% exo-type norbornene derivatives were used. It contains aryl sulfonyl azide group as coupling site of the backbone. Since norbornene derivatives has highly strained structure, initially we applied Grubbs 1st generation catalyst as an initiator for ring-opening metathesis polymerization (ROMP). It produced polymer having molecular weight (M_n) of 8.9k and PDI of 1.37. (Table Ⅳ-1, entry 1) Obviously, fast-initiaing Grubbs 3rd catalyst (Ru-PyCl) produced more controlled polymers having narrow PDI of 1.05 to 1.06. (Table Ⅳ-1, entries 2 and 3)

Although preparing polymer backbone was successful, alkene end

group arising from the quenching of ROMP by addition of ethyl vinyl ether was not proper end for analysis of functionalization. Therefore, we tethered non-invasive functional group containing silyl ether by terminating with *cis*-olefin.[11] (Scheme Ⅳ-1) End-functionalization was confirmed through α position proton of initiating phenyl group, and found that silyl ether group cooperated with above 99%.



Scheme Ⅳ-1. Termination of polymerization for end-group analysis

With this sulfonyl azide polymer in hand, we explored multi-graft polymer using different combination of macromonomers as side chain component. By using slight excess of macromonomers (1.1 eq), sulfonyl azide functional group on preformed polymer was fully converted when detecting azide region in FT-IR. Moreover, it was well correlated with ^{1}H NMR spectrum analysis showing above 99% conversion. Coupling second and third generation of Fréchet dendron with first generation dendron produced dendronized polymers having two different sized of dendron. (Table Ⅳ-2, entries 1 and 2) Graft-to method allowed polymers with Fréchet dendron and polystyrene side chain as well. (Table Ⅳ-2, entry 3) Interestingly, combination of hydrophilic PEG and hydrophobic polystyrene was also possible to

Table Ⅳ-2. Synthesis of various multi-graft polymers

Entry	Prepolymer	Alkyne	Amine	M_n[a] (MALLS)[b]	PDI[a]	Func.[c]
	Oxanorb 30			9.1k	1.05	
1	Oxanorb 30	Fréchet G2	Fréchet G1	22.9k (88.7k)	1.06	>99%
2	Oxanorb 30	Fréchet G3	Fréchet G1	30.2k (234.3k)	1.08	>99%
3	Oxanorb 30	Fréchet G3	PS 2k	30.5k (206.1k)	1.11	>99%
4	Oxanorb 30	PEG 2k	PS 2k	16.5k (n.d.)	1.12	>99%
	Exo-norb 30			8.9k	1.06	
5	Exo-norb 30	Fréchet G3	Fréchet G1	26.7k	1.16	>99%
6	Exo-norb 30	Fréchet G3	Fréchet G2	29.8k	1.14	>99%
7	Exo-norb 30	Ether G2	Fréchet G2	31.1k	1.47	>99%
8	Exo-norb 30	Ether G3	PS 2k	27.0k	2.27	>99%
9	Exo-norb 30	PS 2k	PEG 1k	25.5k	1.19	>99%

[a] Determined by THF SEC calibrated using polystyrene standards [b] Absolute molecular weights (g/mol) determined by THF size-exclusion chromatography (SEC) using MALLS detector. [C] Functionalization efficiency determined by FT-IR and ^{1}H NMR spectrum.

produce polymers of distinct properties. (Table Ⅳ-2, entry 3)

This Janus type of side chain combination also can be coupled on polynorbornene with the combination of non-polar Fréchet type Dendron or polystyrene with relatively polar ether dendron. (Table Ⅳ-2, entries 7 and 8)

Moreover, the dispersity of graft polymers, ranging 1.06 to 1.19, remained as narrow as prepolymer have. This means that

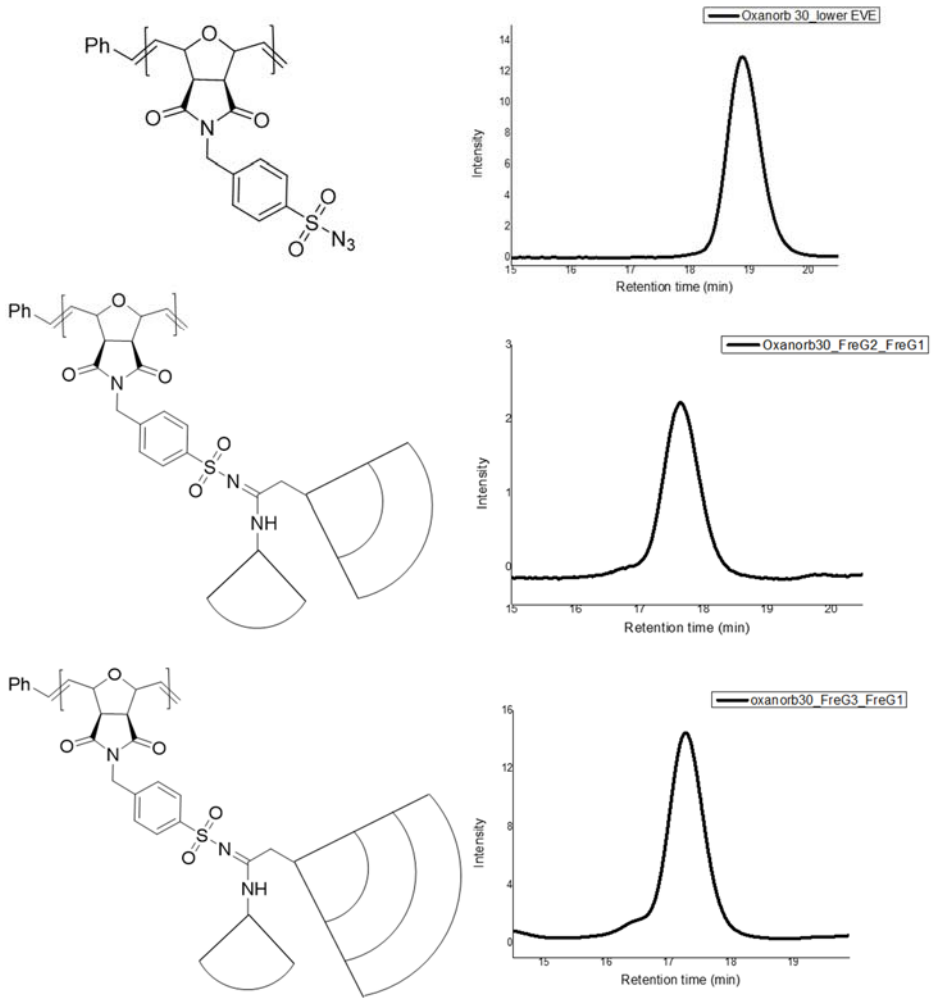


Figure Ⅳ-3. SEC traces of Fréchet type multi-graft polymers

chain-transfer reaction doesn't occur during polymerization, even though there are full of functional groups in combination of different macromonomers. Also, SEC traces of each multi-graft polymers showed single modal distribution, supporting that this polymerization is highly selective and efficient. However, even though dendronized macromonomers have perfect structures, if some macromonomers

already have distribution (such as the case of polymer macromonomers), the final multi-graft polymers have the tendency of slight broadening. Also, properties and steric hinderance of side chain is important, causing different interaction toward polystyrene standard.

3. Conclusion

Through versatility of Cu-catalyzed MCP, we envisioned that different combination of side chains and dendrons can be applied to the single polymer chain to produce multi-graft polymers. Diversity-oriented synthesis is still major roles on this type of polymerization. Moreover, two distinct mono-functionalized macromonomers enrich polymer architectures and properties, paving the way of easy synthesis of future functional materials, such as photonic crystals or multi-response materials.

Experimental Section

General Experimental

Techniques

NMR spectra were recorded by Varian/Oxford As-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C), Agilent 400-MR DD2 Magnetic Resonance System (400 MHz for ^{1}H, 100 MHz for ^{13}C), Bruker DRX-300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) spectrometers. UV-vis spectra were measured by Jasco Inc. UV/vis-Spectrometer V-550. The molar masses of macromonomers were measured by Bruker Daltonics autoflex II TOF/TOF. Dithranol in THF was used as a matrix. THF Gel permeation chromatography (GPC) for polymer molecular weight analysis was carried out with Waters system (1515 pump, 2414 refractive index detector and 2489 UV detector) and Shodex GPC LF-804 column eluted with THF (GPC grade, Honeywell Burdick & Jackson). Flow rate was 1.0 mL/min and temperature of column was maintained at 35 ° C. Samples were diluted in 0.001-0.005 wt% by THF and filtered with a 0.20 μm PTFE filter before injection into the GPC. For the MALLS-VIS-RI analysis, Wyatt triple detector and Dawn 8^{+} / Viscostar II / Optilab T-rEX were used. Chloroform Gel permeation chromatography (GPC) for polymer molecular weight analysis was carried out with Waters system (1515 pump, 2414 refractive index detector and 2489 UV detector) and Shodex GPC LF-804 column eluted with chloroform

(HPLC grade, J. T. Baker). Flow rate was 1.0 mL/min and temperature of column was maintained at 35 ° C. Samples were diluted in 0.001−0.005 wt% by chloroform and filtered with a 0.20 μm PTFE filter before injection into the GPC. For the MALLS−VIS−RI analysis, Wyatt triple detector and Dawn 8^+ / Viscostar II / Optilab T−rEX were used. Flow rate was 1.0 mL/min and temperature of column was maintained at 35 ° C. Samples were diluted in 0.001−0.005 wt% by chloroform and filtered with a 0.20 μm PTFE filter before injection into the GPC. For the MALLS−VIS−RI analysis, Wyatt detector and Dawn 8^+ / Optilab T−rEX were used. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out unde r N_2 gas at a scan rate of 10 ° C/min with Q50 and Q10 model devices, respectively, from TA Instruments.

Materials

Without additional notes, all reagents were commercially available and used without further purification. DCM and TEA were distilled over CaH_2, and THF was distilled over sodium and benzophenone. 1,2−DCE, 1,4−dioxane, DMF, DIPEA, pyridine were purified by solvent purification system using alumina column. All solvents and bases were degassed by argon bubbling for 10 minutes before using on polymerization without further purification.

Chapter Ⅱ - Experimental

Synthetic procedure for diyne preparation

1,4-bis(hex-5-ynyloxy)benzene (1b)

: This monomer was prepared by the method from the previous literature.1 1H-NMR, 13C-NMR and MS analysis data are also available in the same literature.

4,4' -bis(pent-4-ynyloxy)biphenyl (1c)

: This monomer was prepared by the method from the previous literature.2 1H-NMR, 13C-NMR and MS analysis data are also available in the same literature.

1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene(1d)

: This monomer was prepared by slightly modified method from the previous literature.3 1H-NMR, 13C-NMR and MS analy-sis data are also available in the same literature.

1,5-bis(hex-5-ynyloxy)naphthalene (1e)

: This monomer was prepared by the method from the previous literature.1 1H-NMR, 13C-NMR and MS analysis data are also available in the same literature.

General synthetic procedure for sulfonyl azides (2a−2f)

: To a stirred solution of sulfonyl chloride (20 mmol, 1.0 eq) in acetone (100 mL), a solution of sodium azide (30 mmol, 1.5 eq) in water (100 mL) was added dropwise at 0° C. The reaction was allowed to warm up to room temperature and stirred un−til sulfonyl chloride was consumed up. The acetone was removed under reduced pressure at 25 ° C and the reaction mixture was extracted with dichloromethane twice. The combined organic layer was dried over MgSO4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatograph on silica gel to afford a correspond−ing sulfonyl azide (quantitative yield). Compounds were previously reported; (2f)4, (2e)5, (2a, 2d)6, (2c, 2b)7

Synthetic procedure for diol preparation

(1r,4r)−cyclohexane−1,4−diyldimethanol (3b)

: This monomer was prepared by slightly modified method from the previous literature.8 1H−NMR 13C−NMR, MS, and IR analysis data are also available in the same literature.

2,2−dibutylpropane−1,3−diol (3d)

: This monomer was prepared by slightly modified method from the previous literature.9 1H−NMR and MS analysis data are also

available in the same literature.

2,2-dibenzylpropane-1,3-diol (3e)

: This monomer was prepared by slightly modified method from the previous literature.10 1H-NMR, 13C-NMR, MS, and IR analysis data are also available in the same literature.

(1R,2S,3R,4S)-bicyclo[2.2.1]hept-5-ene-2,3-diyldimethanol (3g)

: This monomer was prepared by slightly modified method from the previous literature.11 1H-NMR and 13C-NMR analysis data are also available in the same literature.

(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)dimethanol (3h)

: To a flask charged with diethyl 2,5-dihydroxyterephthalate hydroquinone (3i), (2.54 g, 10 mmol), potassium carbonate (4.15 g, 30 mmol), KI(10 mol%) in acetone (30 mL), 2-ethylhexyl bromide (4.45 mL, 25 mmol) was added. The reaction mixture was refluxed for 18 h. The mixture was diluted with DCM, then washed with water and saturated NaCl solution. The aqueous layer was extracted with DCM twice. The combined organic layers were dried over MgSO4 and concentrated under reduced pressure. The crude residue was redissolved in anhydrous THF (30 mL), then LiAlH4 (1.14g, 30mmol) was added portionwise at 0 oC. The reaction mixture was warmed to room temperature and stirred for 4 h. After quenching by adding of cold water, the separated organic layer was washed with brine and extracted with DCM twice. The combined extracts were dried and

evaporated under reduced pressure. It was purified by flash column chromatography on silica gel (Hexane : EtOAc = 4 : 1) to afford compound 3h as a white solid (2.92 g, 74%). Rf = 0.35 (Hexane : EtOAc = 4 : 1). 1H NMR (300 MHz, CDCl3) : δ 6.87 (s, 2H), 4.69–4.66 (d, 4H), 3.89–3.87(d, 2H), 2.36–2.31(t, 2H), 1.76–1.66(m, 2H), 1.53–1.38(m, 8H), 1.33–1.30(m, 8H), 0.96–0.88(m, 12H) ; 13C NMR (75 MHz, CDCl3): δ 150.68, 129.01, 111.95, 70.96, 61.96, 39.60, 30.75, 29.13, 24.15, 23.09, 14.12, 11.22; HRMS (FAB+) : calculated for C24H42O4, 394.3083, observed, 394.3087.

Polymerization procedure for the model polymer D

: p-toluenesulfonyl azide 2a (3 eq) was slowly added into the mixture of diyne 1b (1 eq), diol 3a (1 eq), and Cu(I) catalyst (10 mol%) in tested solvent, and then the additive was added. The polymerization underwent for 48 h under Ar atmosphere. The resulting mixture was precipitated into MeOH.

General polymerization procedure

: Sulfonyl azide (3 eq) was slowly added into the mixture of diyne (1 eq), diol (1 eq), and CuCl (10 mol%) in DCM at r.t., and then triethylamine (5 eq) was added. The polymerization underwent at room temperature for 48 h under Ar atmosphere. In some cases, the addition sequence of sulfonyl azide and diamine was reversed due to the states of monomers. The result-ing mixture was precipitated into MeOH. The resulting polymers were dissolved in CHCl3 or DMF, and passed through the short neutral alumina column to remove the

residual copper. Then, those were precipitated again into MeOH to ensure com-plete removal of monomers, and dried under vacuum, which afforded pale green solid (entries 10-14, 16, 17, 21), dark green solid (entries 5 and 6), olive-green solid (entries 1-3, 15, 18, 19, 22), pale or dark brown solid (entries 4, 7, 20, 23), and sticky brown solid (entries 8 and 9).

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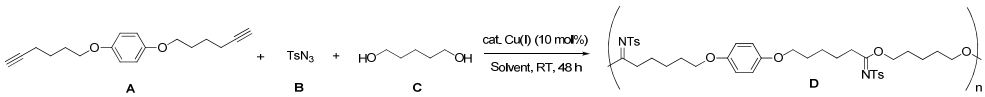
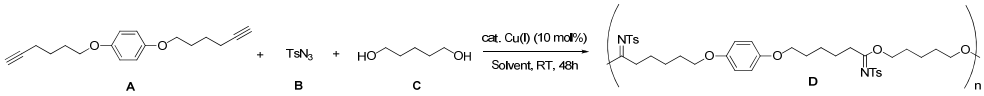
MCP optimization for the model polymer D



Entry	Catalyst	Solvent	Base (eq)	Temp (°C)	Additive (eq)	M_w (PDI)[a]
1	**CuCl**	**DCM**	**TEA (5)**	**RT**	**None**	**16.6k (2.37)**
2	CuCl	DCM	TEA (5)	40	None	8.5k (1.48)
3	CuCl	$CHCl_3$	TEA (5)	RT	None	13.2k (2.17)
4	CuCl	$CHCl_3$	TEA (5)	45	None	12.3k (1.79)
5	CuCl	$CHCl_3$	TEA (5)	reflux	None	8.3k (1.52)
6	CuCl	DCE	TEA (5)	RT	None	7.9k (1.59)
7	CuCl	DCE	TEA (5)	45	None	15.1k (2.37)
8	CuCl	DCE	TEA (5)	70	None	14.3k (2.03)
9	CuCl	THF	TEA (5)	RT	None	8.7k (1.94)
10	CuCl	THF	TEA (5)	45	None	9.2k (1.58)
11	CuCl	THF	TEA (5)	reflux	None	8.4k (1.62)
12	CuCl	DMF	TEA (5)	70	None	6.2k (1.48)
13	CuCl	DMSO	TEA (5)	70	None	5.9k (1.52)
14	CuCl	1,4-dioxane	TEA (5)	70	None	14.0k (3.19)
15	CuI	$CHCl_3$	TEA (5)	RT	None	12.8k (2.35)
16	CuBr	$CHCl_3$	TEA (5)	RT	None	11.9k (1.70)
17	$CuBrSMe_2$	$CHCl_3$	TEA (5)	RT	None	10.6k (1.74)
18	$CuBr(PPh_3)_3$	$CHCl_3$	TEA (5)	RT	None	8.4k (1.54)
19	CuCl	DCM	TEA (5)	RT	TBTA (0.1)	6.5k (1.58)
20	CuCl	DCM	TEA (5)	RT	DMAP (0.1)	4.0k (1.43)

[a] Determined by THF SEC calibrated by polystyrene standards

Base screening for the MCP



entry	catalyst	solvent	base (eq)	temp	additive	M_w (PDI)[a]
1	CuCl	DCM	Trioctylamine (5)	RT	None	13.5k (2.21)
2	CuCl	DCM	DIPEA (5)	RT	None	10.6k (1.84)
3	CuCl	DCM	Proton sponge (5)	RT	None	5.5k (1.53)
4	CuCl	DCM	2,6-Lutidine (5)	RT	None	10.3k (2.39)
5	CuCl	DCM	Pyridine (5)	RT	None	6.8k (1.60)
6	CuCl	DCM	Imidazole (5)	RT	None	No polymer
7	CuCl	DCM	DBU (5)	RT	None	No polymer
8	CuCl	DCM	K_2CO_3 (5)	RT	None	No polymer
9	CuCl	DCM	Cs_2CO_3 (5)	RT	None	No polymer

[a] Determined by THF SEC calibrated by polystyrene standards.

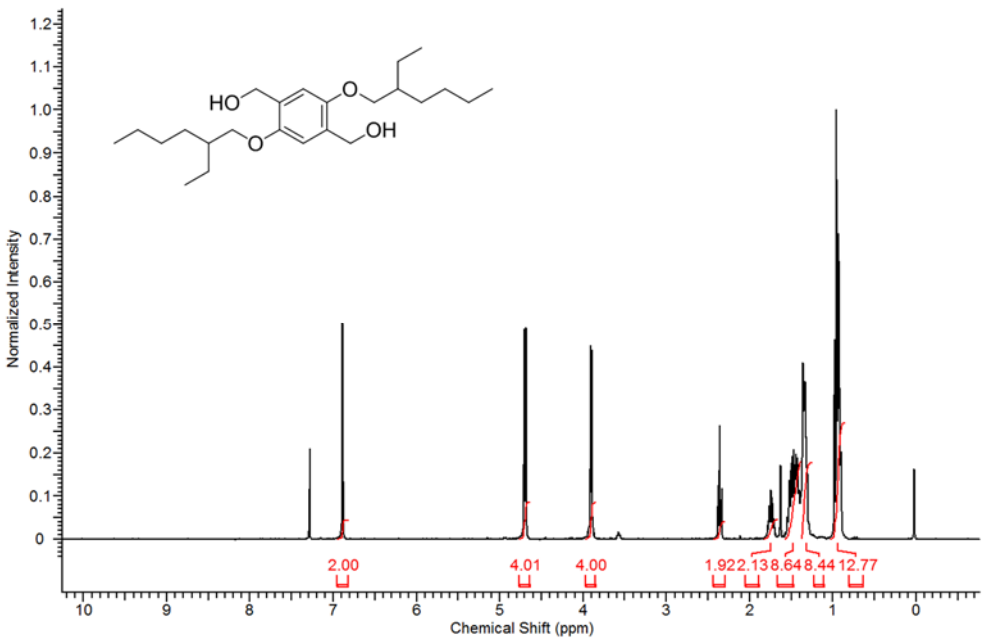
Degree of polymerization (DP) calculated by ^{1}H NMR

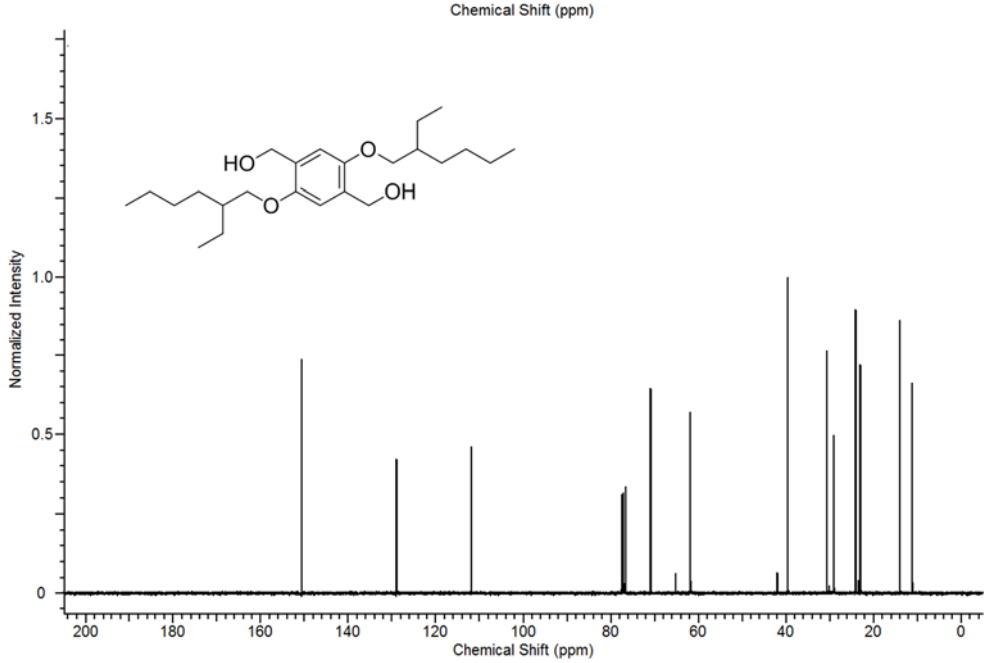
polymer	Repeat unit mass	DP(NMR)	MW(NMR)	M_n[a]	M_w[a]
Table 2, entry 1	562.74	9.1	5.1k	5.8k	11.2k
Table 2, entry 2	712.92	8.5	6.1k	7.0k	16.6k
Table 2, entry 3	760.96	8.8	6.7k	9.5k	17.4k
Table 2, entry 5	752.98	8.1	6.1k	6.2k	12.8k
Table 2, entry 6	737.02	6.4	4.7k	4.5k	10.7k
Table 2, entry 7	860.92	8.5	7.3k	6.8k	10.5k
Table 2, entry 10	977.40	8.7	8.5k	10.0k	20.2k
Table 2, entry 12	1027.46	8.5	8.7k	10.8k	32.2k
Table 2, entry 13	937.34	19.2	18.0k	9.2k	15.1k
Table 2, entry 14	1012.43	19.5	19.7k	12.4k	28.9k
Table 2, entry 15	1089.53	11.7	12.7k	10.0k	19.7k
Table 2,entry 24	726.94	7.5	5.5k	6.3k	10.9k

Determined by THF SEC calibrated using polystyrene standards.

^{1}H NMR and ^{13}C NMR spectra of monomer

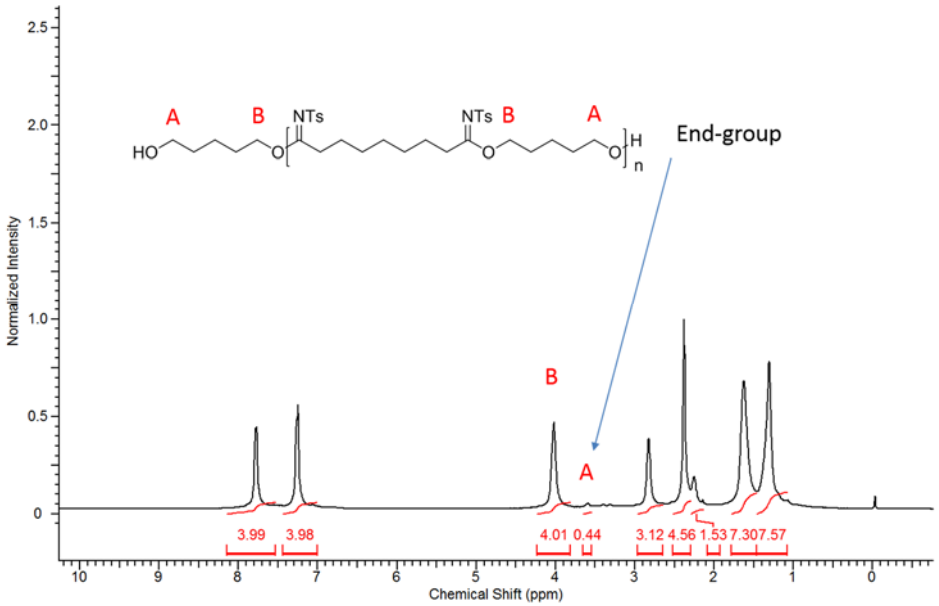
Table Ⅱ-3, 3h ($CDCl_3$)





^{1}H NMR and ^{13}C NMR Spectra of polymers

Table Ⅱ−3, entry 1 ($CDCl_3$)



Degree of Polymerization = (4.01 / number of B) / (0.44 / number of A) = 9.1

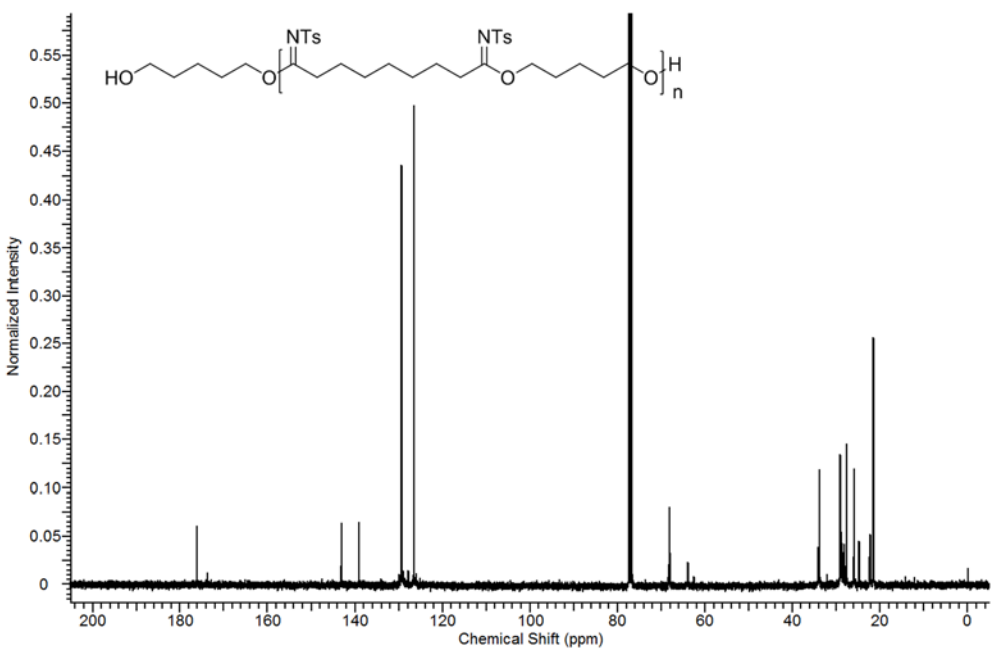
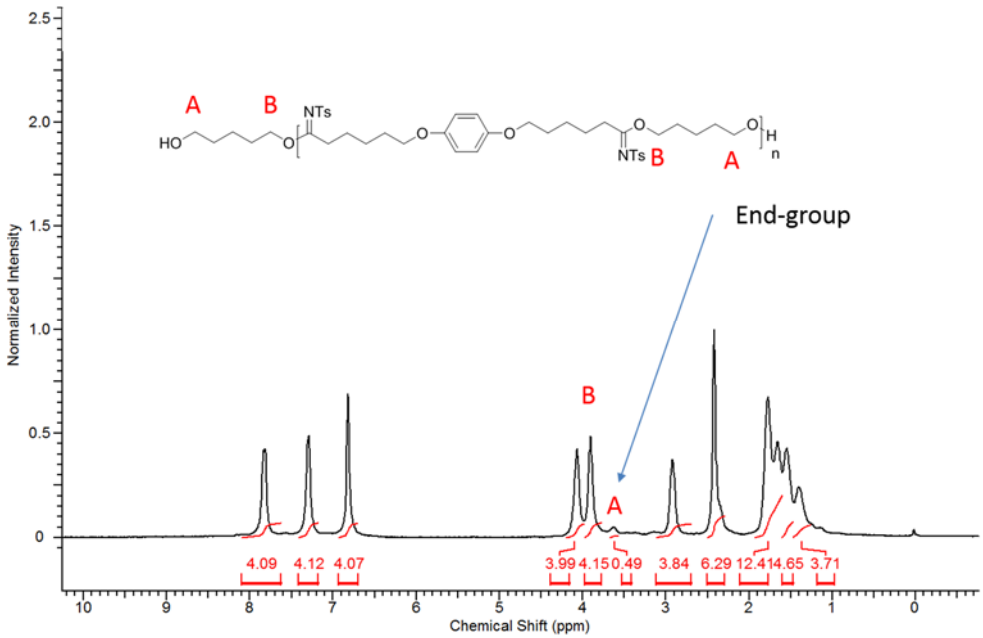


Table Ⅱ－3, entry 2 ($CDCl_3$)



Degree of Polymerization = (4.15 / number of B) / (0.49 / number of A) = 8.5

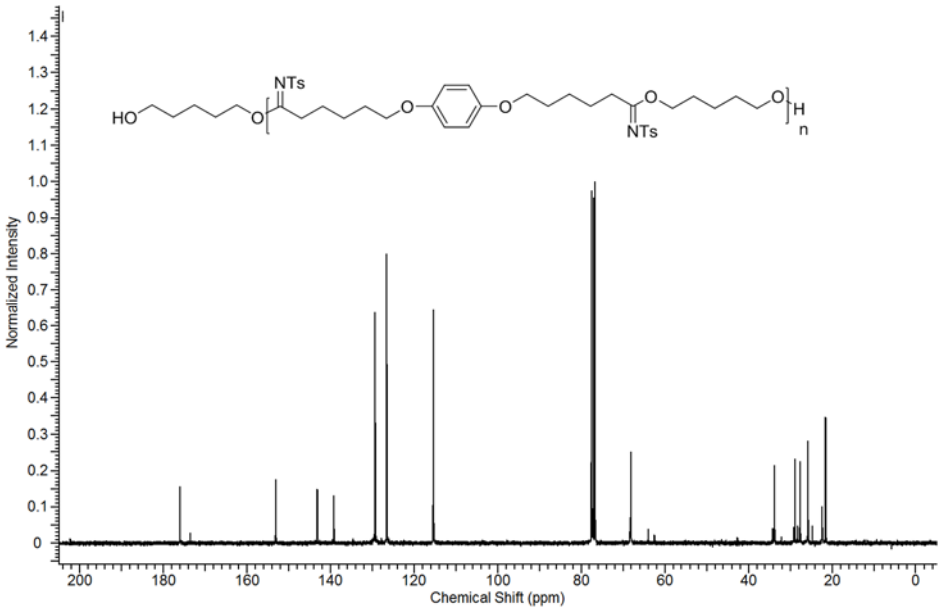
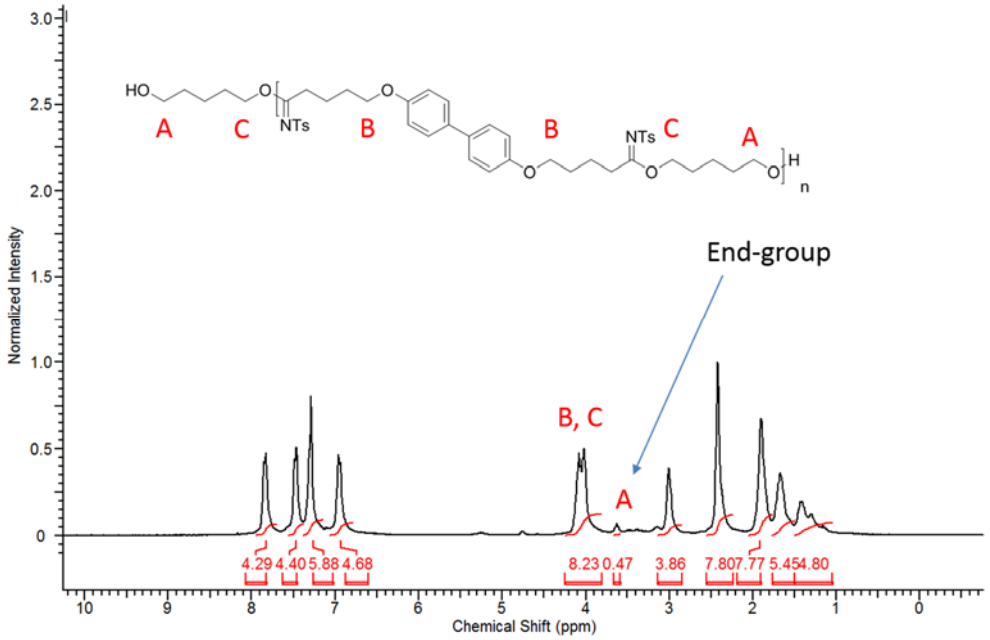


Table Ⅱ－3, entry 3 ($CDCl_3$)



Degree of Polymerization = (8.23 / number of B and C) / (0.47 / number of A) = 8.8

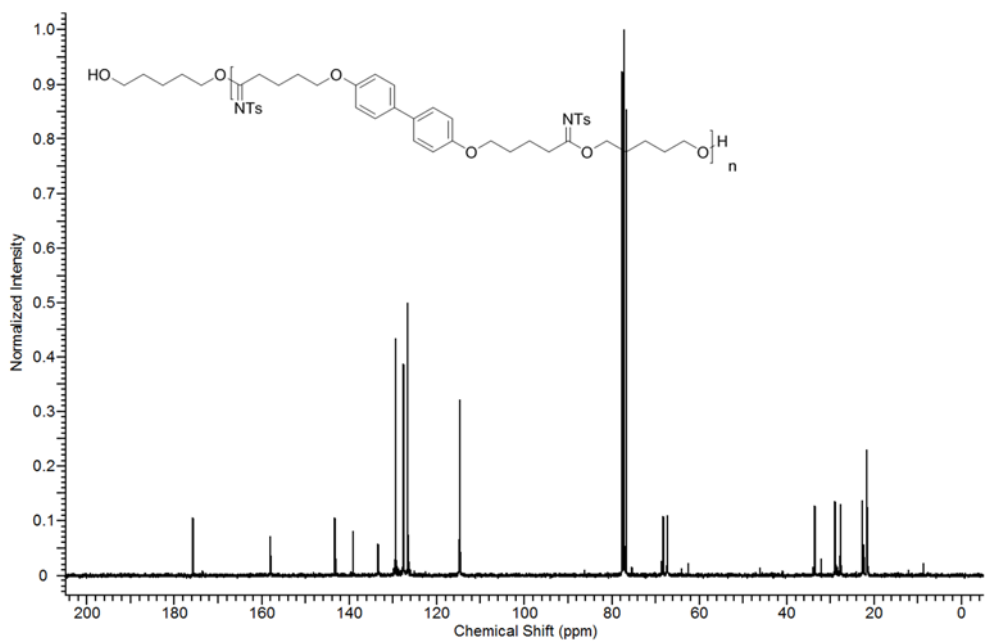
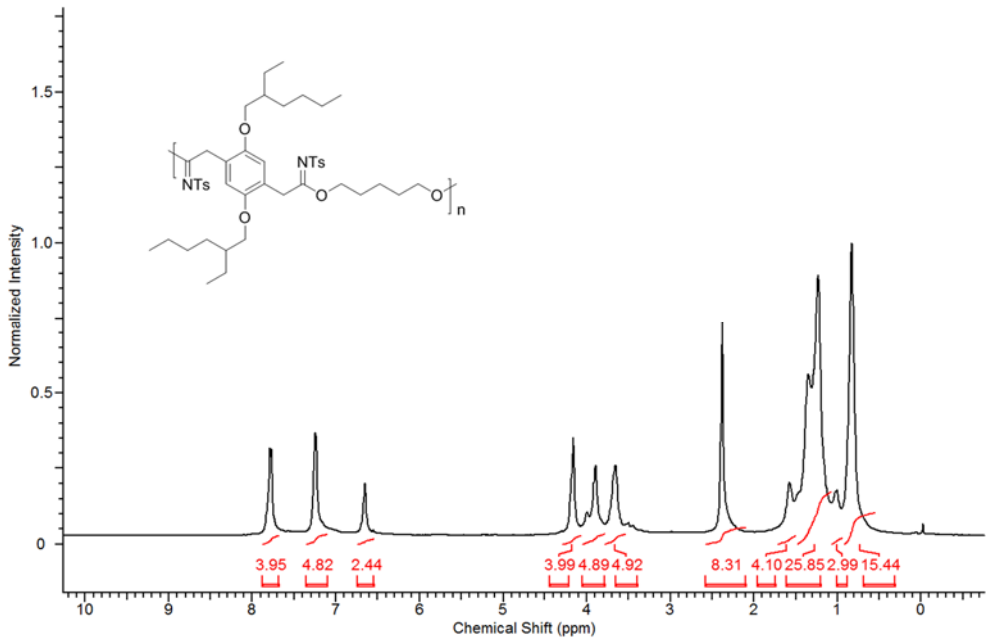


Table Ⅱ−3, entry 4 ($CDCl_3$)



***Overlapped end-group peak**

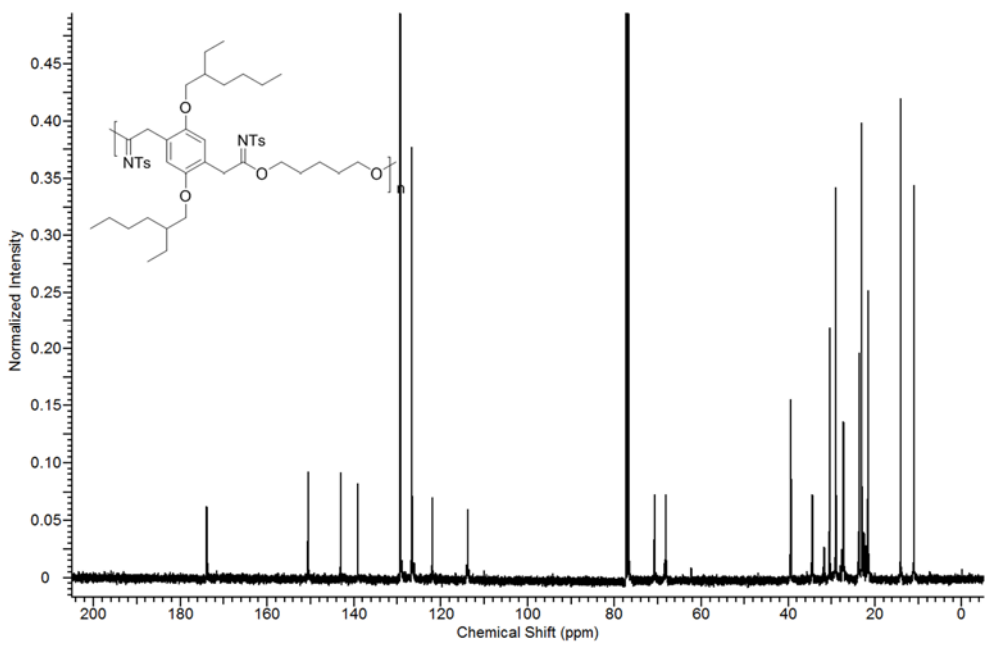
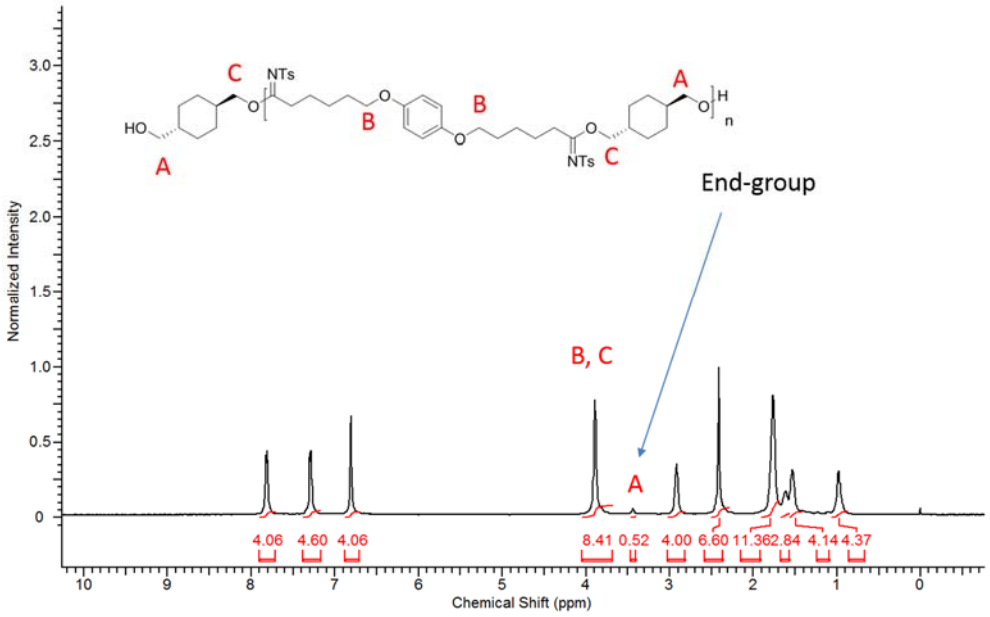


Table Ⅱ－3, entry 5 ($CDCl_3$)



Degree of Polymerization = (8.41 / number of B and C) / (0.52 / number of A) = 8.1

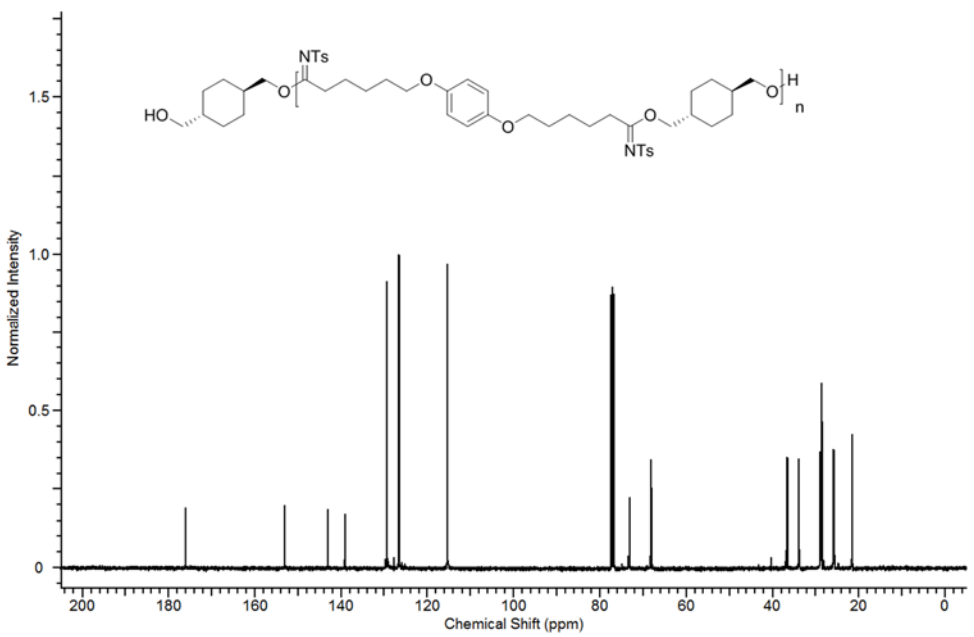
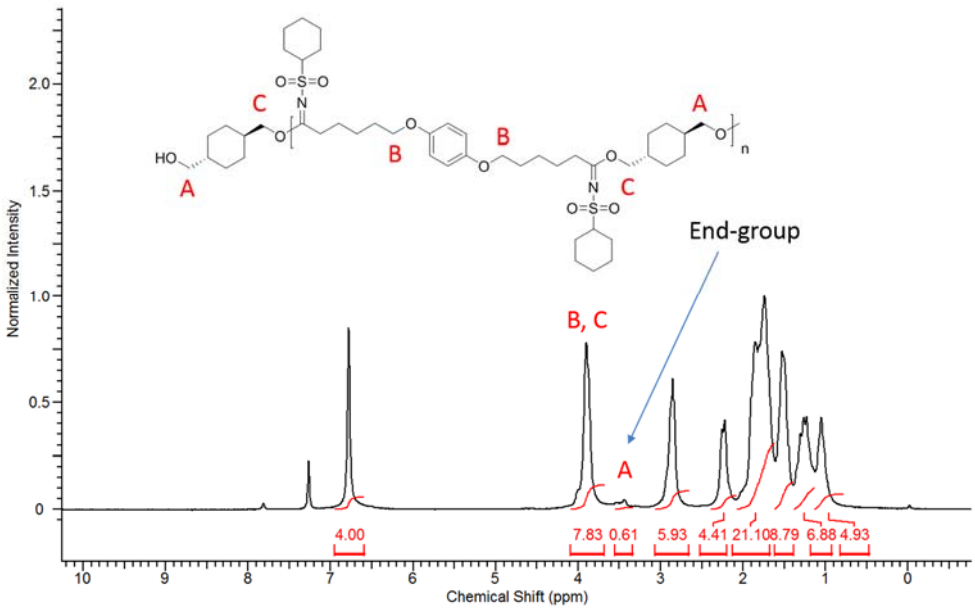


Table Ⅱ－3, entry 6 ($CDCl_3$)



Degree of Polymerization = (7.83 / number of B and C) / (0.61 / number of A) = 6.4

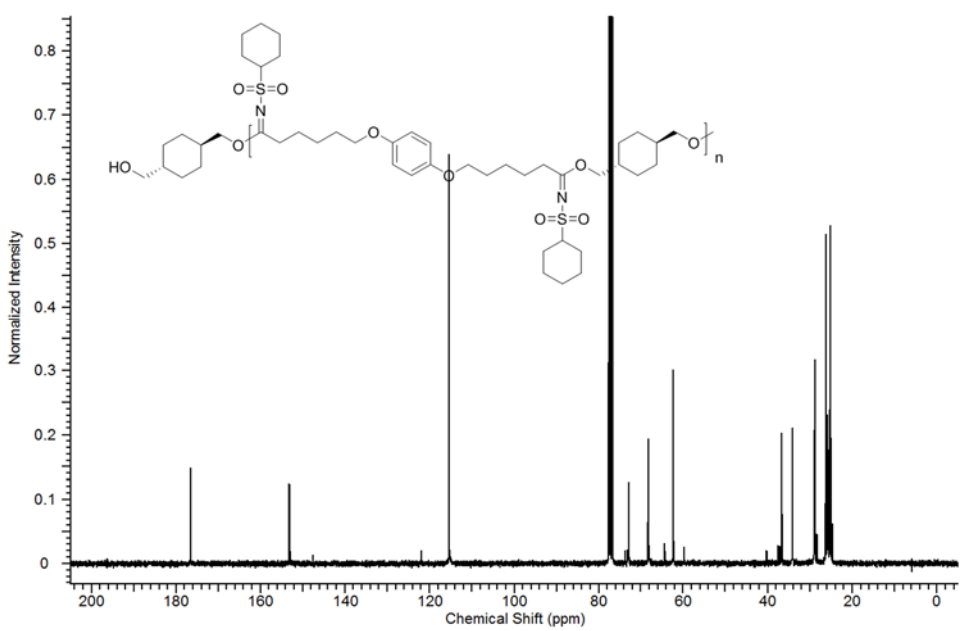
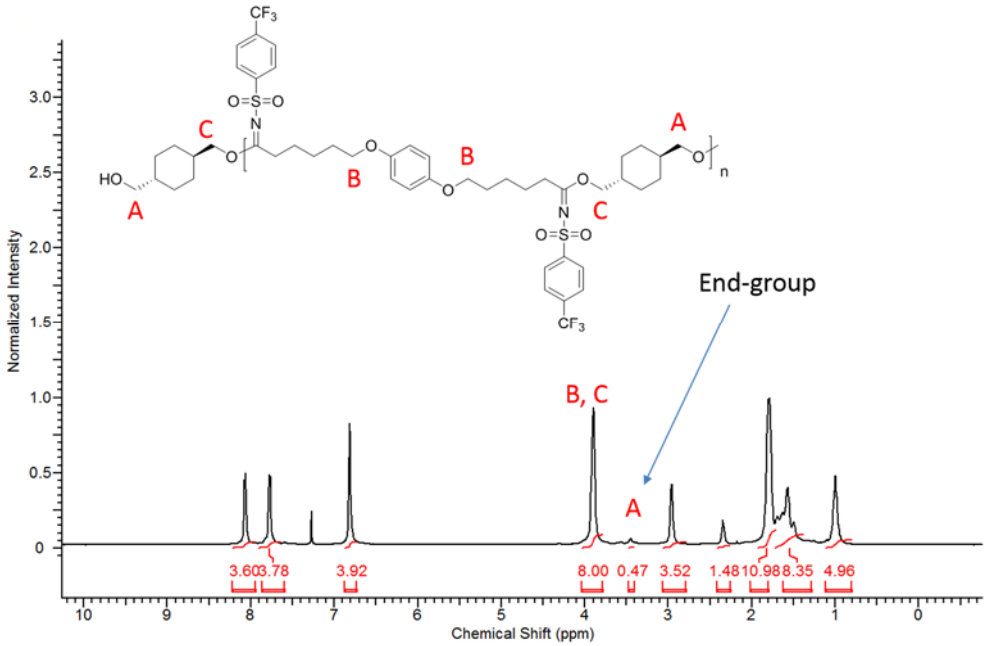


Table Ⅱ－3, entry 7 ($CDCl_3$)



Degree of Polymerization = (8.00 / number of B and C) / (0.47 / number of A) = 8.5

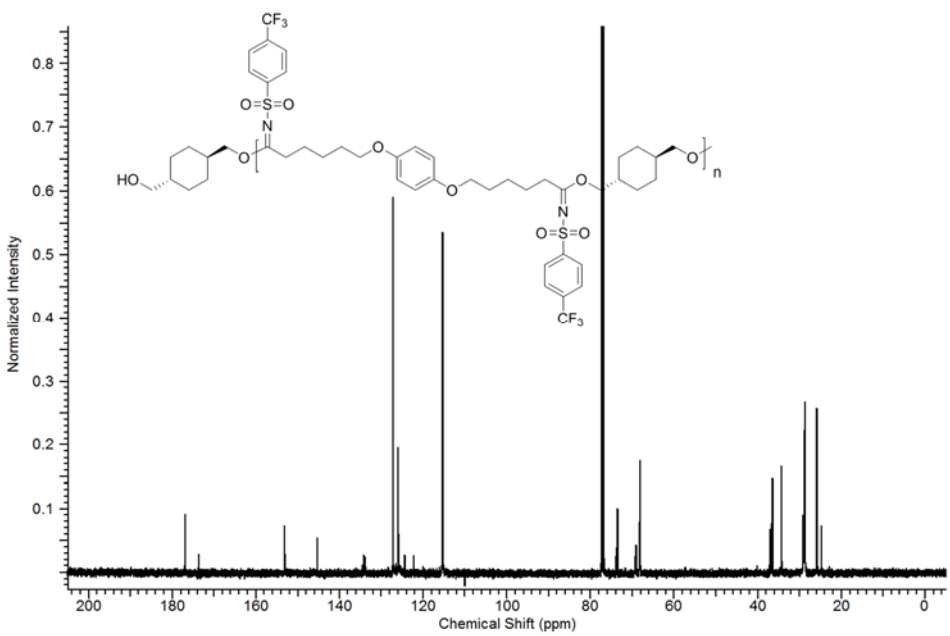
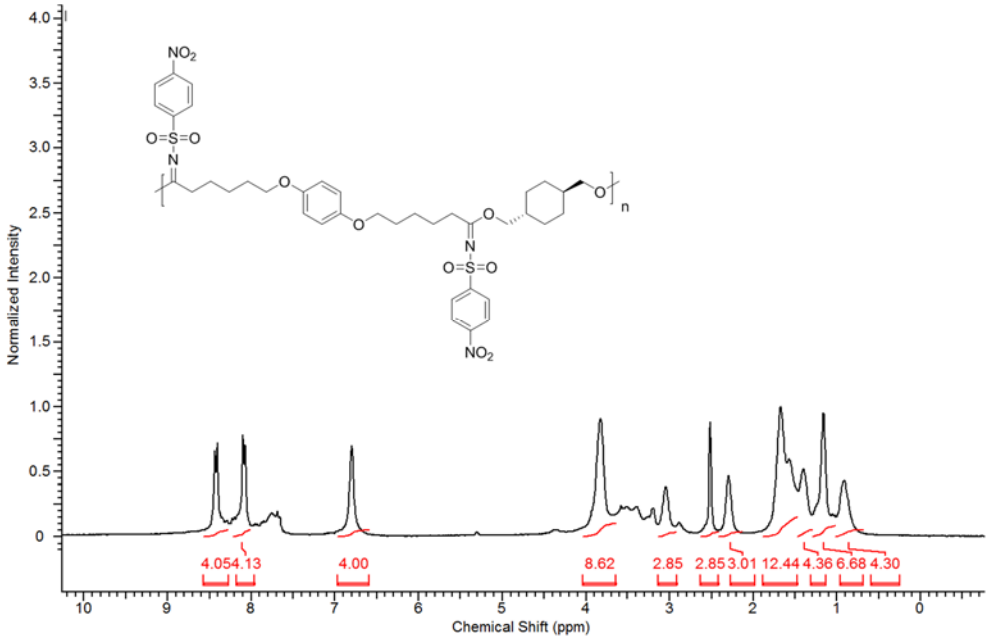


Table Ⅱ-3, entry 8 (DMSO-d_6)



***Overlapped end-group peak**

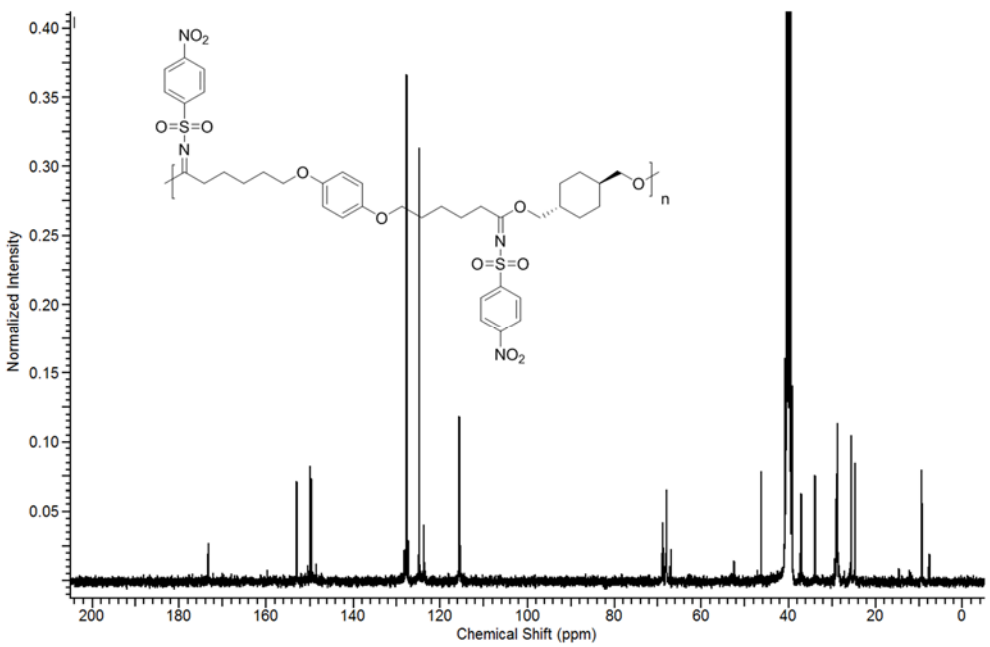
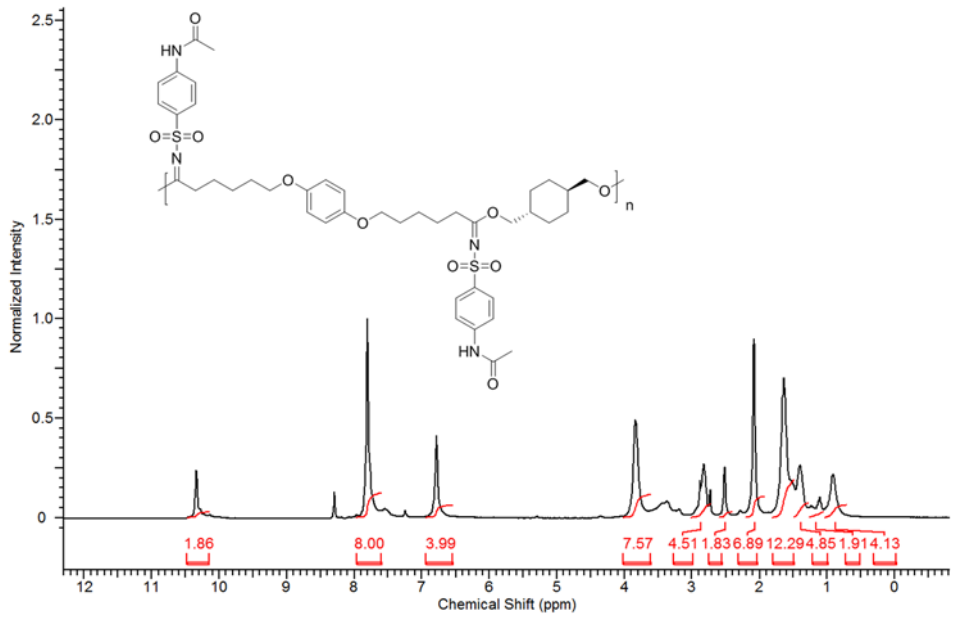


Table Ⅱ-3, entry 9 (DMSO-d_6)



***Overlapped end-group peak**

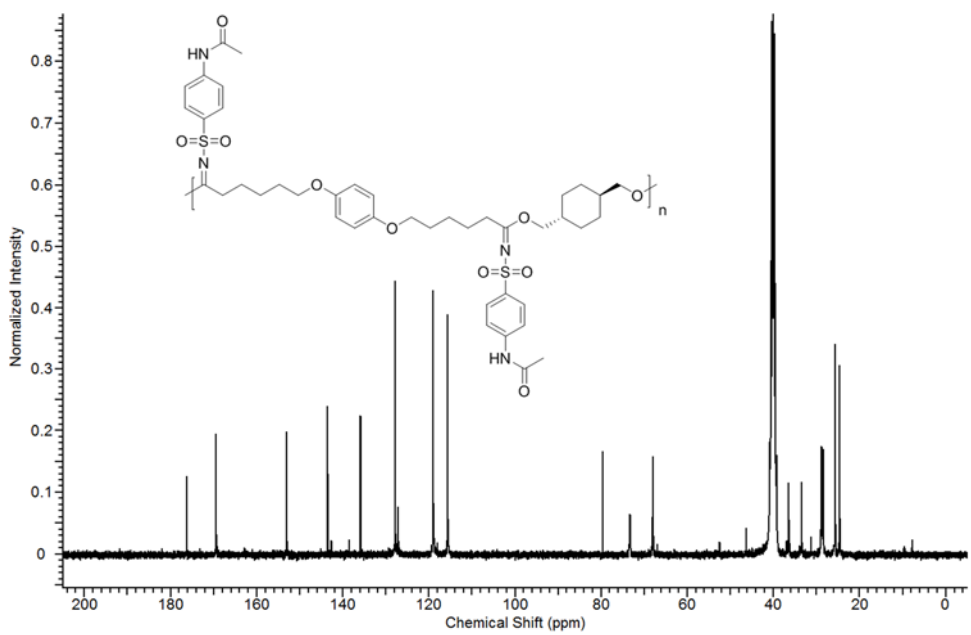
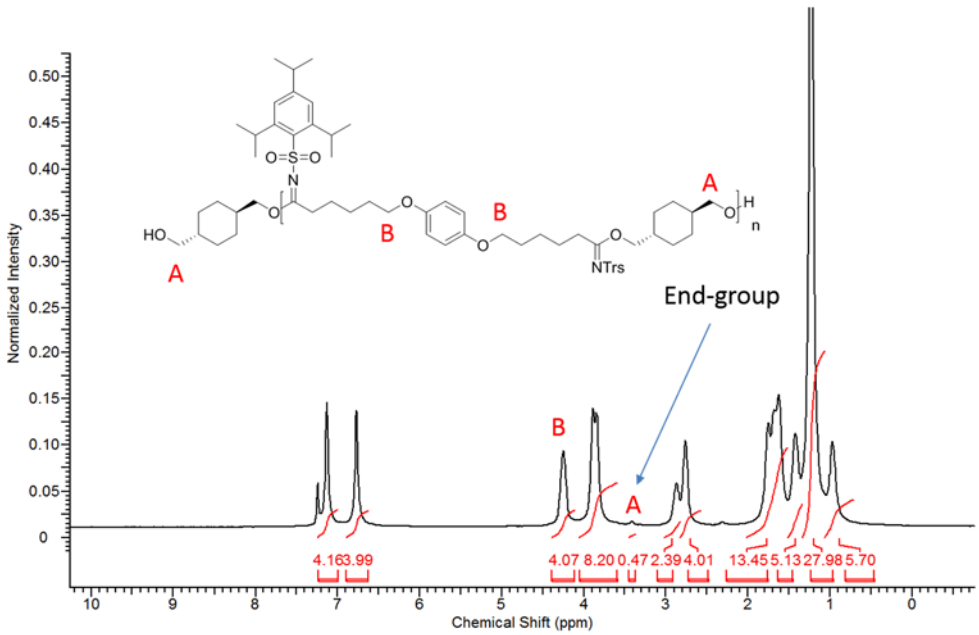


Table Ⅱ－3, entry 10 ($CDCl_3$)



Degree of Polymerization = (4.07 / number of B) / (0.47 / number of A) = 8.7

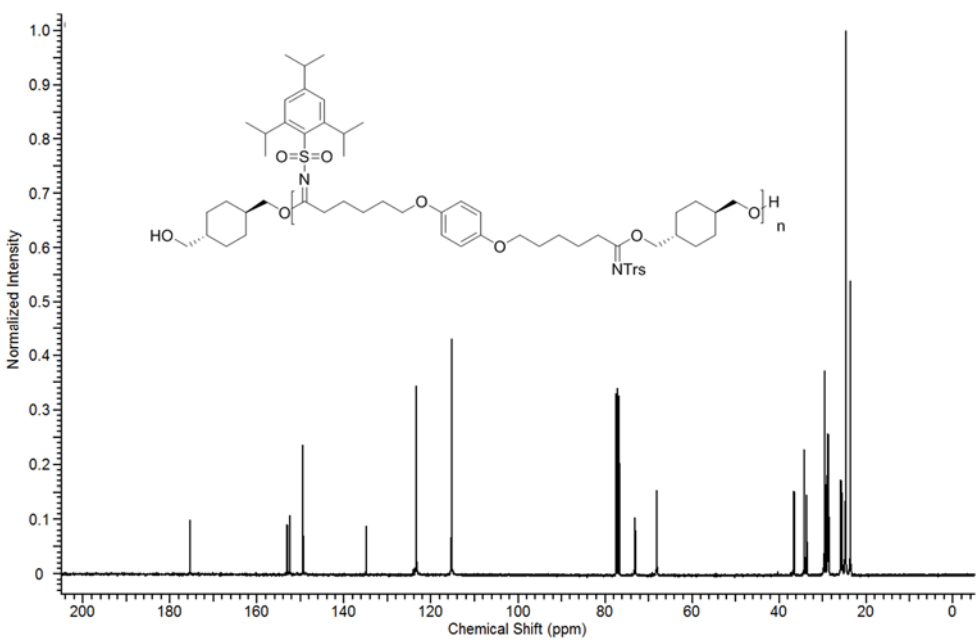
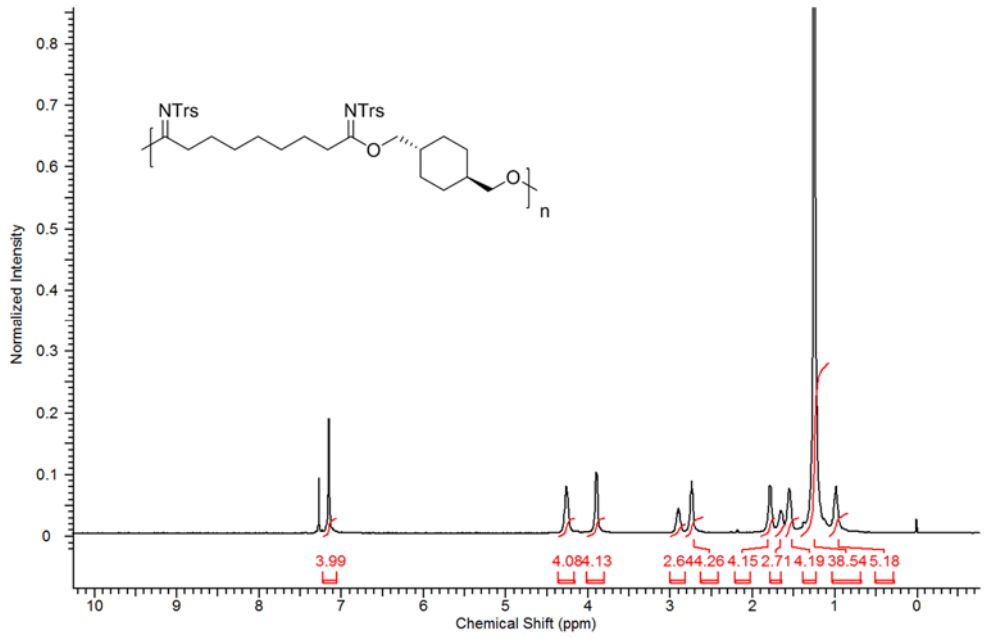


Table Ⅱ−3, entry 11 ($CDCl_3$)



***End-group peak was not observed.**

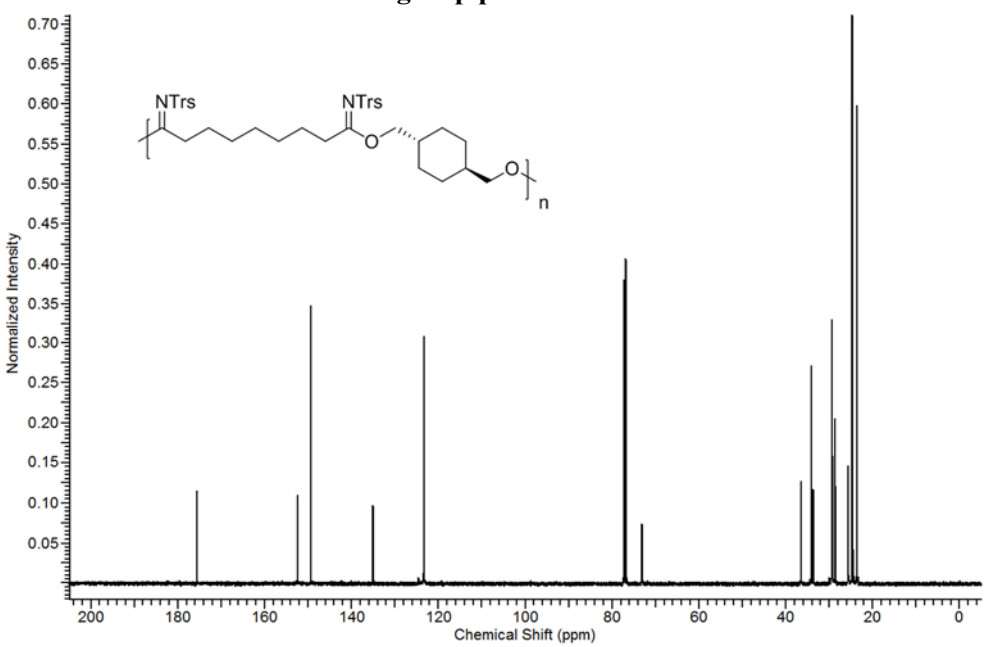
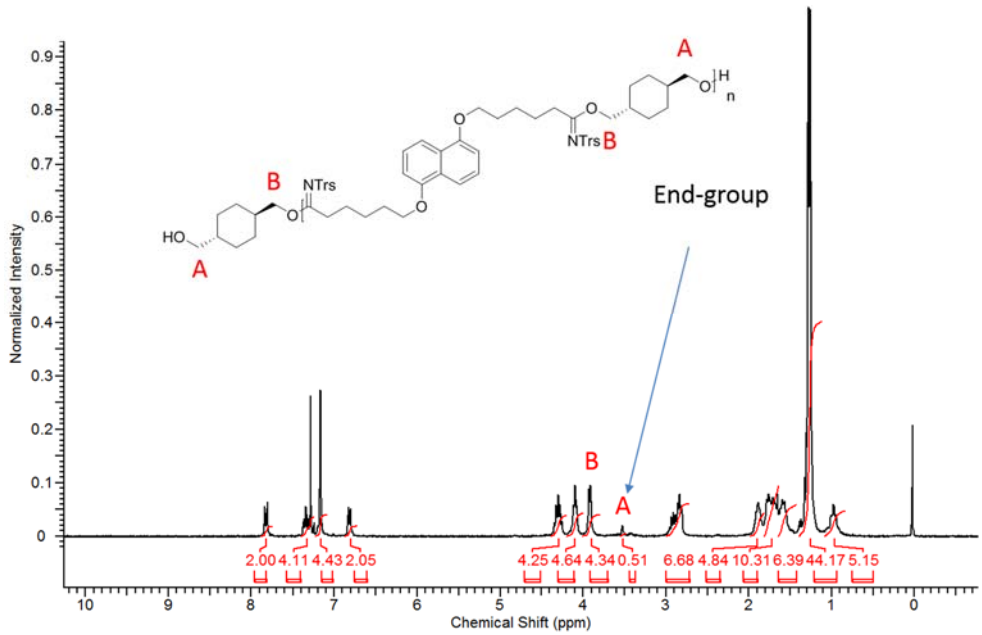


Table Ⅱ−3, entry 12 ($CDCl_3$)



Degree of Polymerization = (4.34 / number of B) / (0.51 / number of A) = 8.5

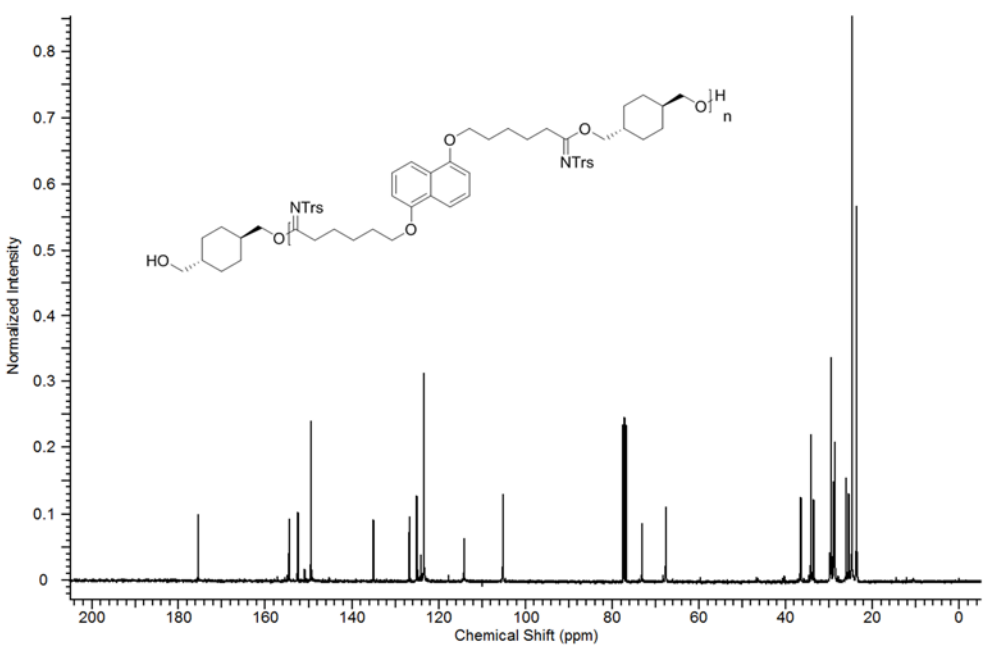
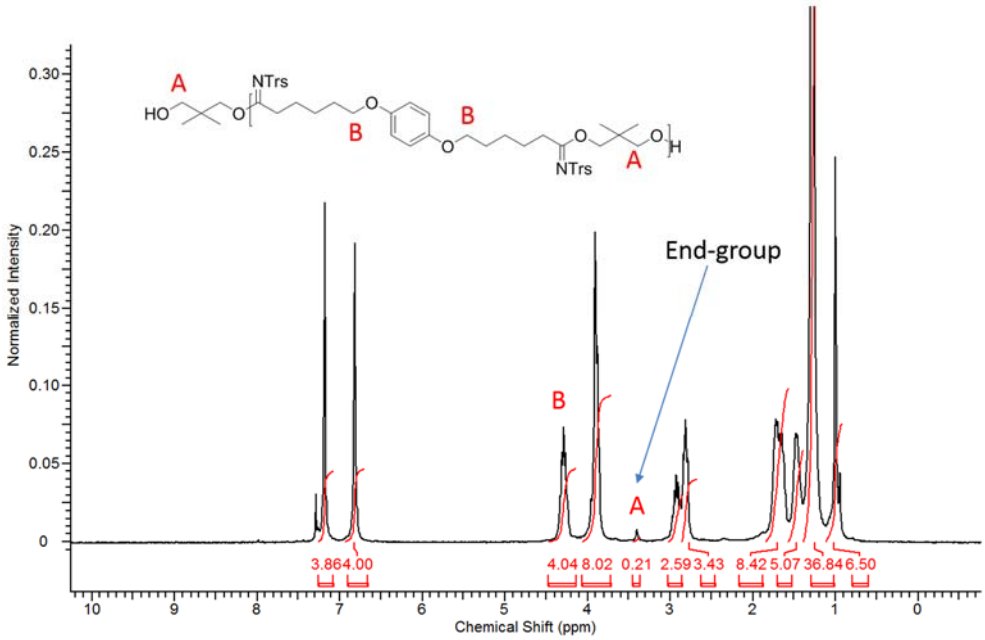


Table Ⅱ-3, entry 13 ($CDCl_3$)



Degree of Polymerization = (4.04 / number of B) / (0.21 / number of A) = 19.2

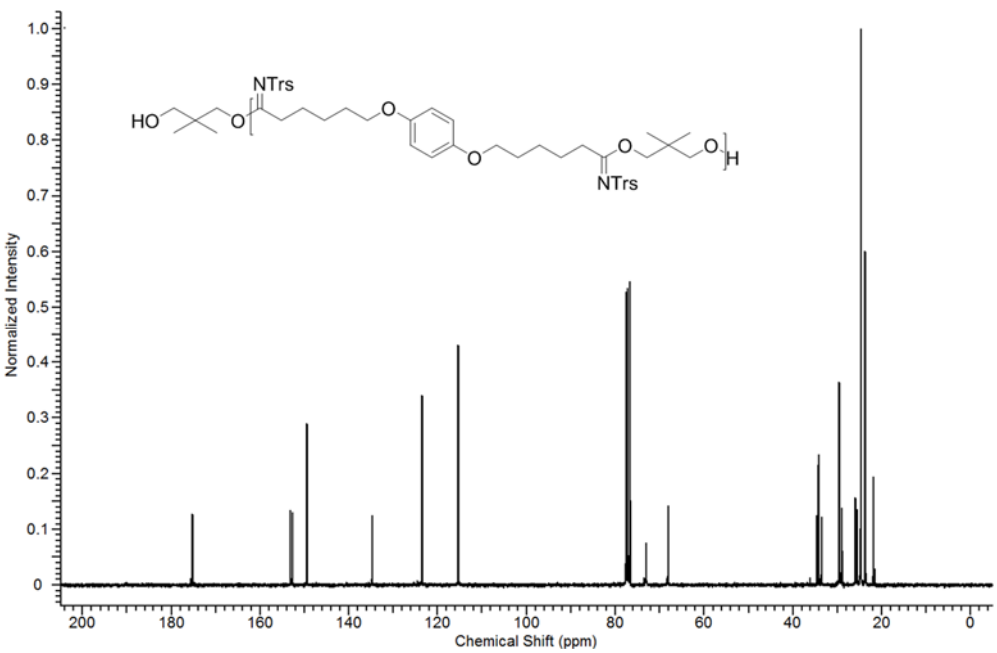
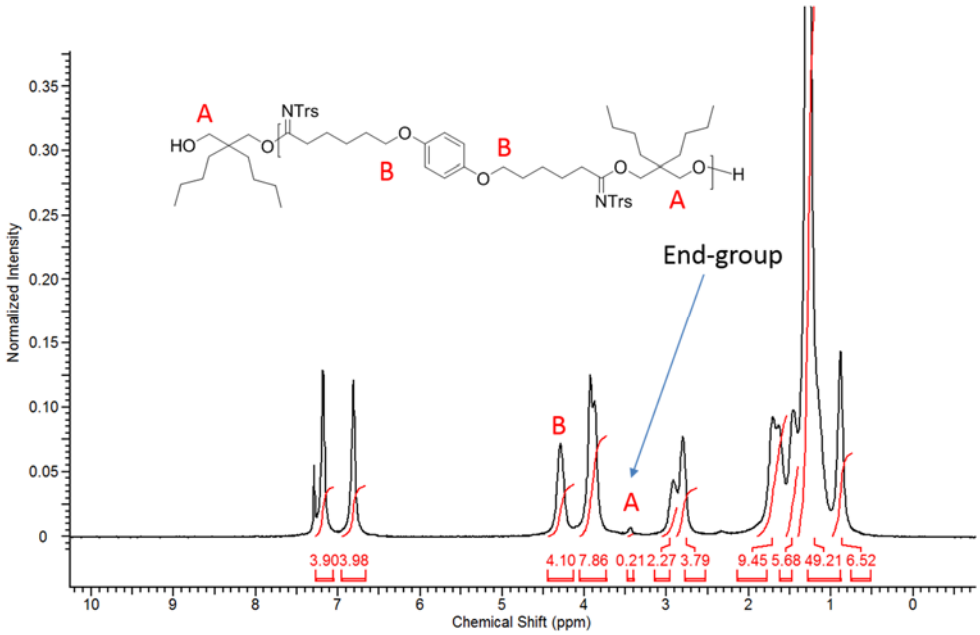


Table Ⅱ－3, entry 14 ($CDCl_3$)



Degree of Polymerization = (4.10 / number of B) / (0.21 / number of A) = 19.5

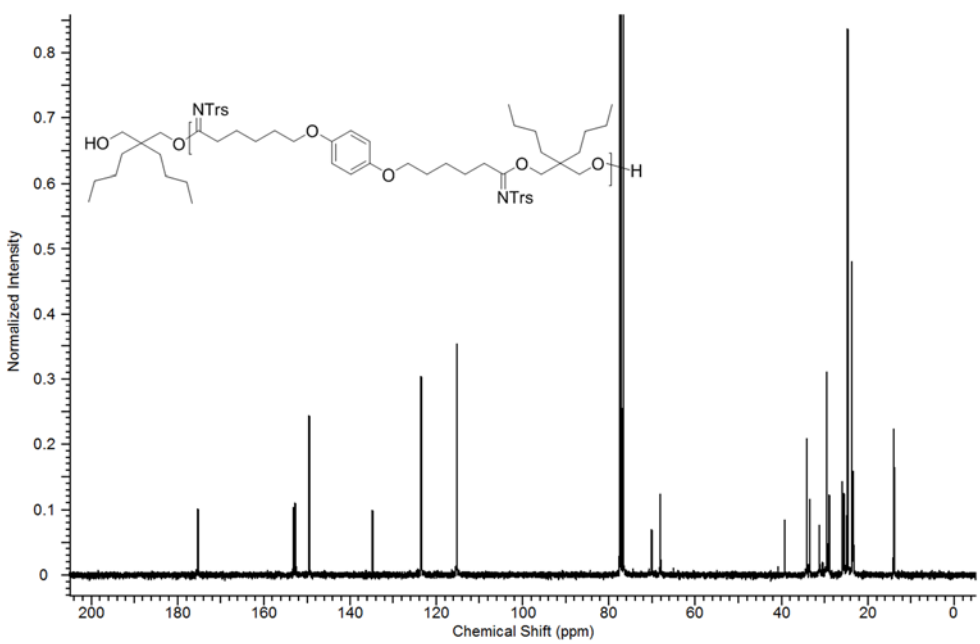
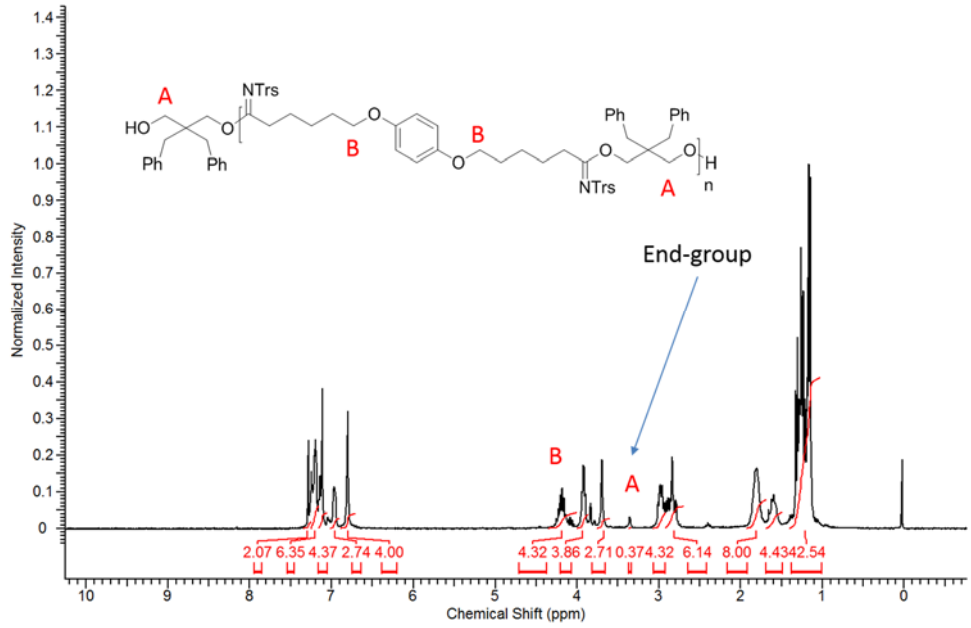


Table Ⅱ－3, entry 15 ($CDCl_3$)



Degree of Polymerization = (4.32 / number of B) / (0.37 / number of A) = 11.7

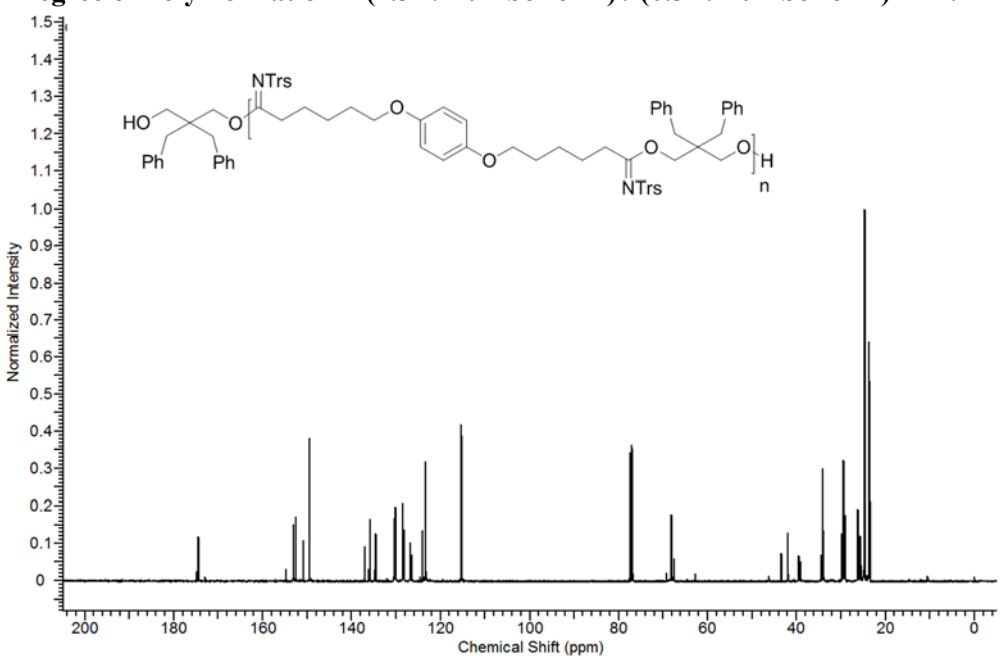
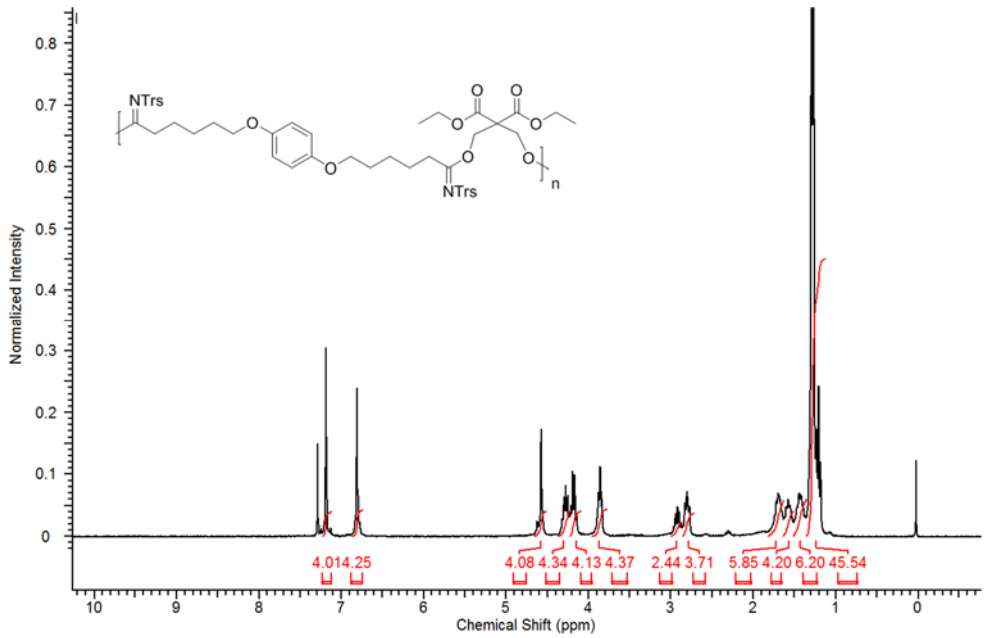


Table Ⅱ−3, entry 16 ($CDCl_3$)



***End-group peak was not observed.**

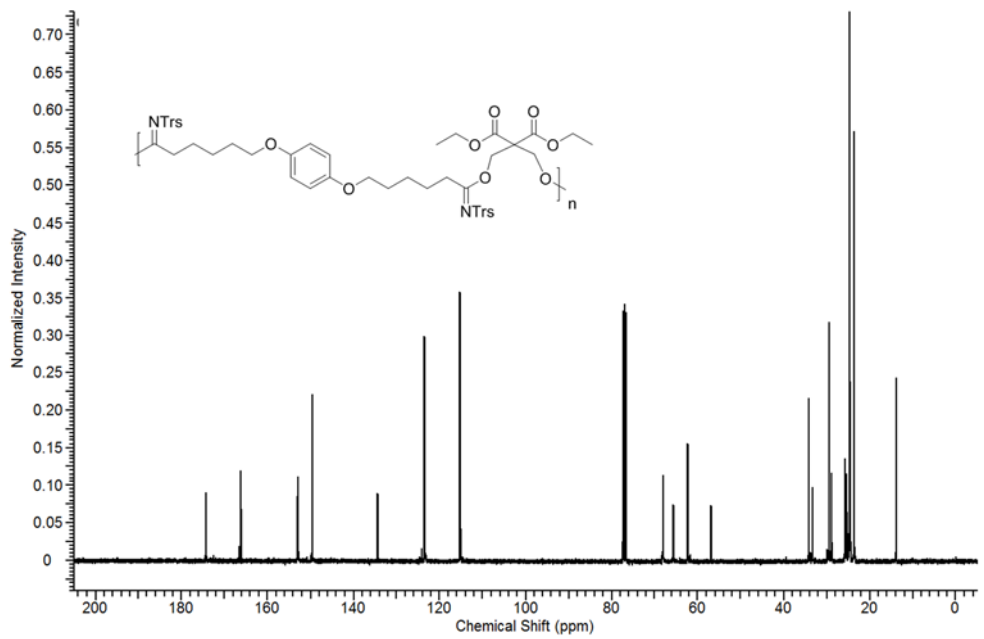
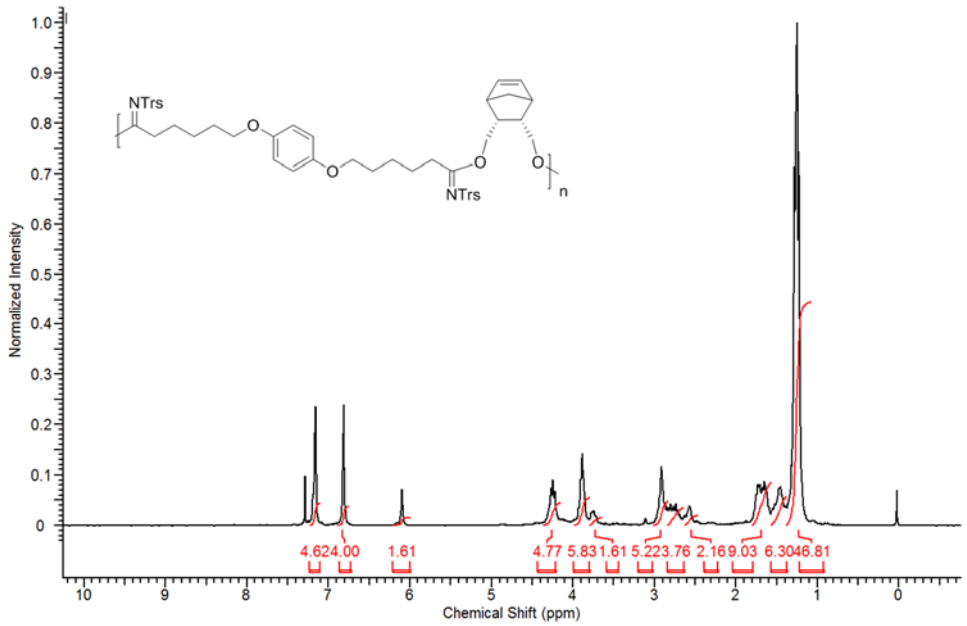


Table Ⅱ−3, entry 17 ($CDCl_3$)



***End-group peak was not observed.**

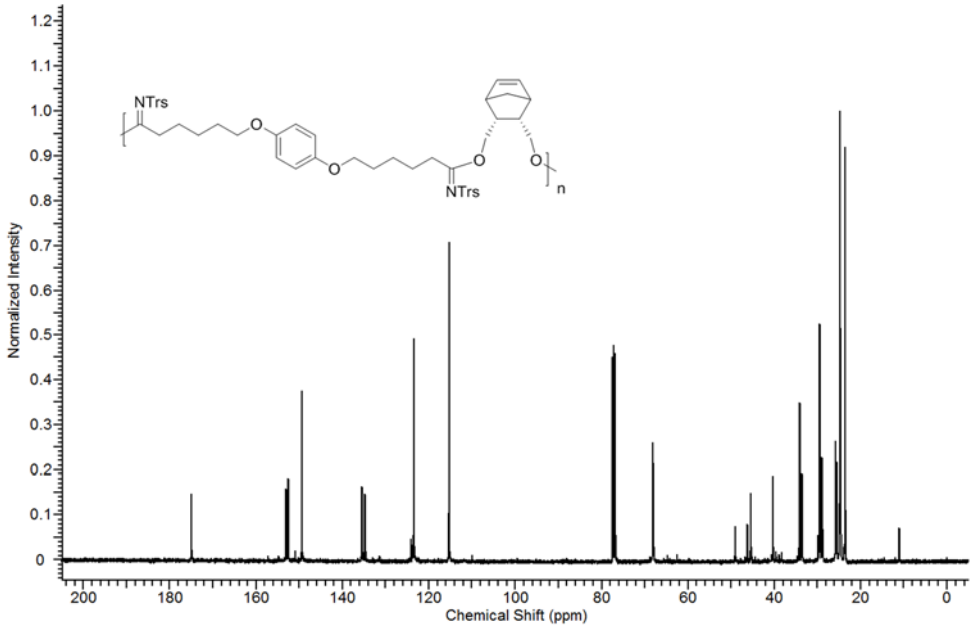
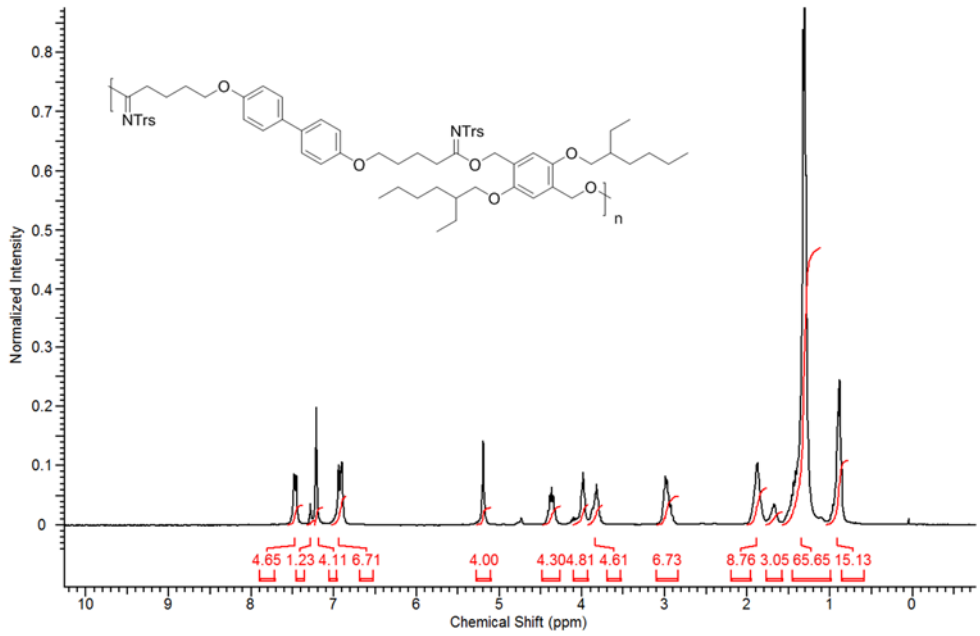


Table Ⅱ−3, entry 18 ($CDCl_3$)



***End-group peak was not observed.**

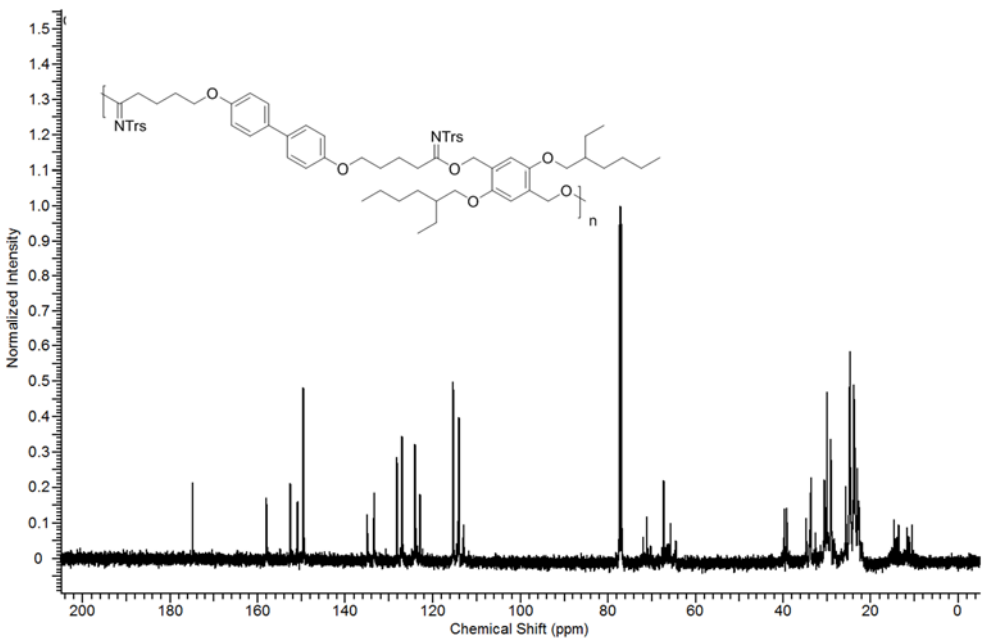
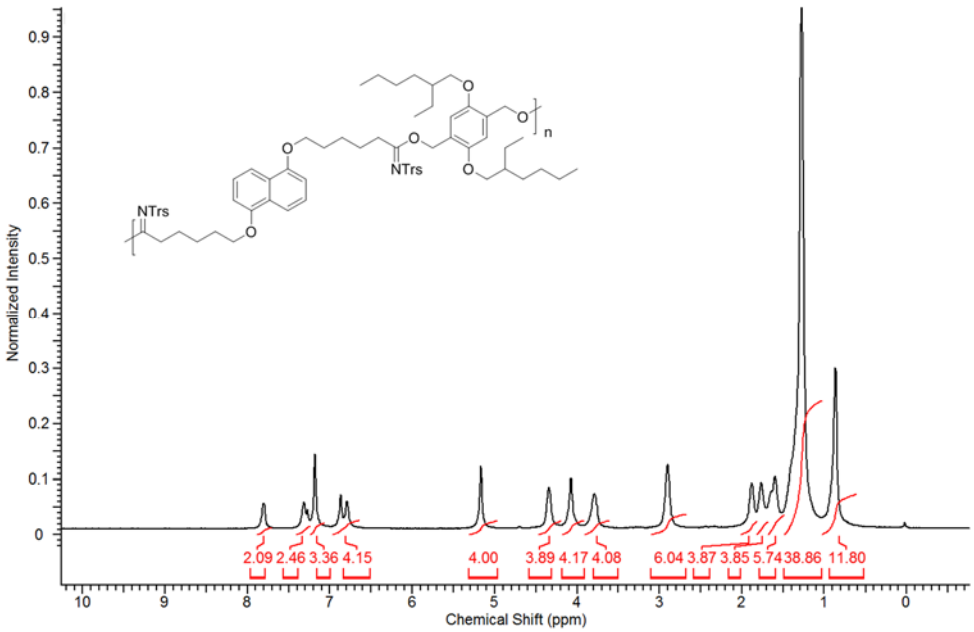


Table Ⅱ−3, entry 19 ($CDCl_3$)



***End-group peak was not observed.**

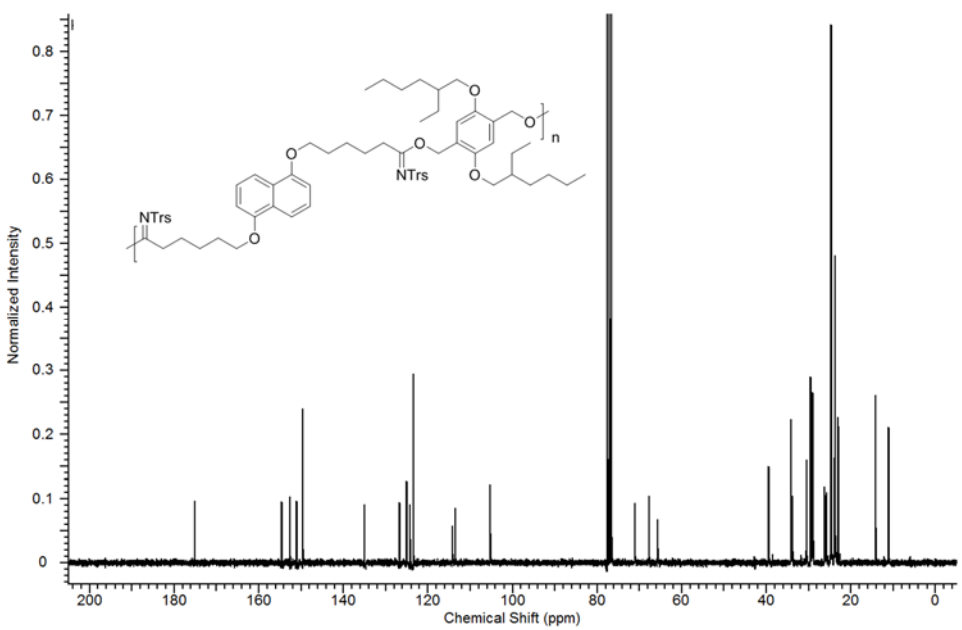
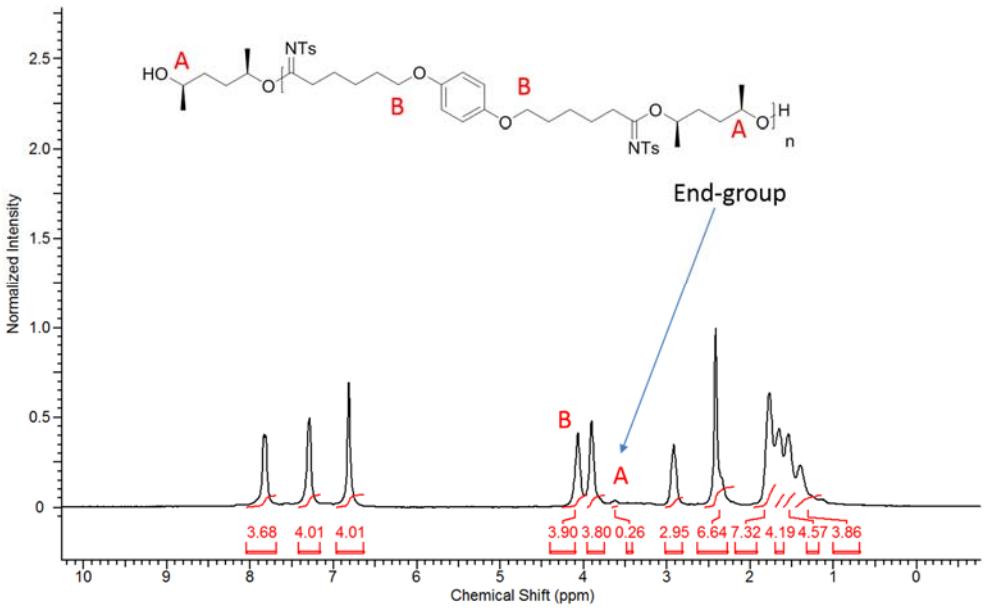


Table Ⅱ-3, entry 20 ($CDCl_3$)



Degree of Polymerization = (3.90 / number of B) / (0.26 / number of A) = 7.5

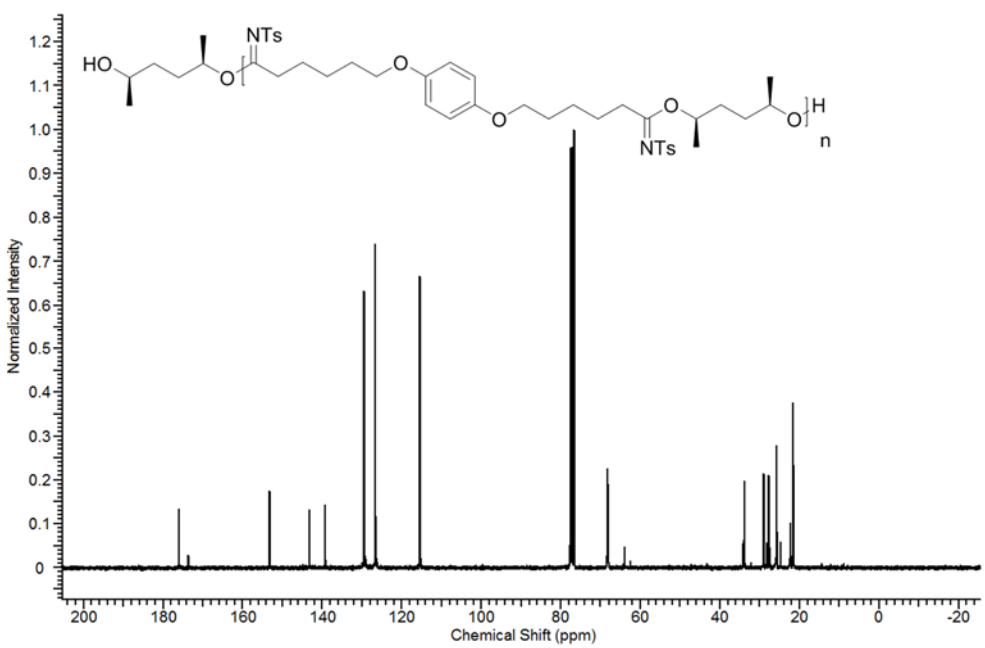
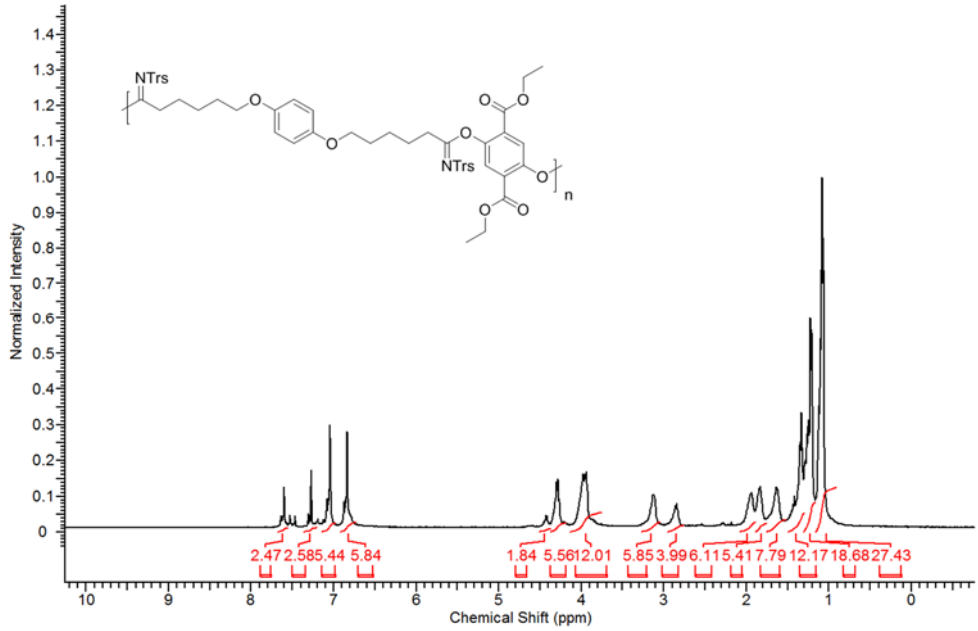


Table Ⅱ−3, entry 21 ($CDCl_3$)



***End-group peak was not observed.**

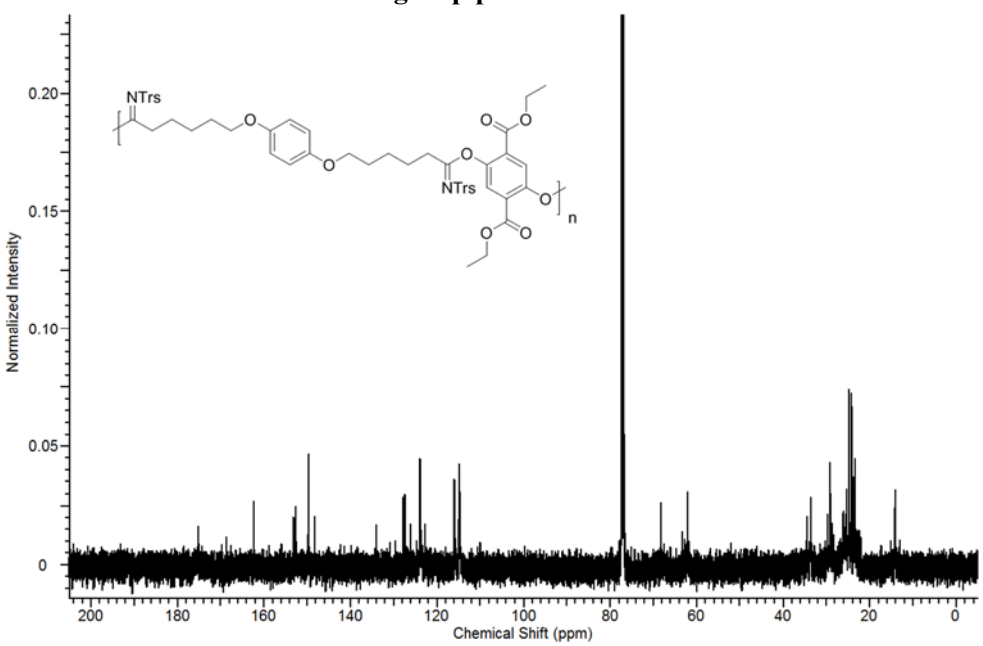
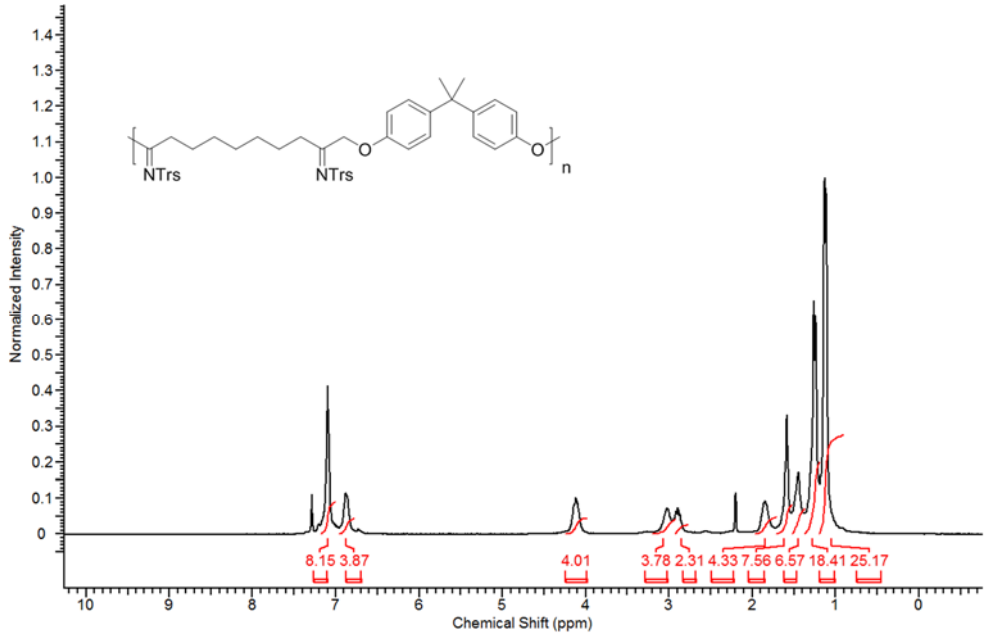


Table Ⅱ－3, entry 22 ($CDCl_3$)



***End-group peak was not observed.**

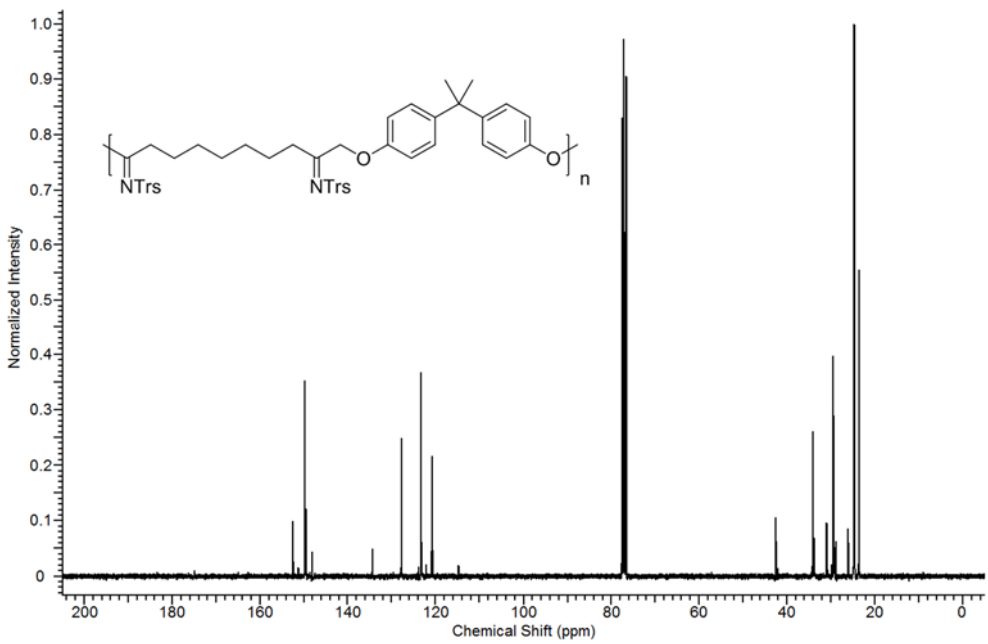
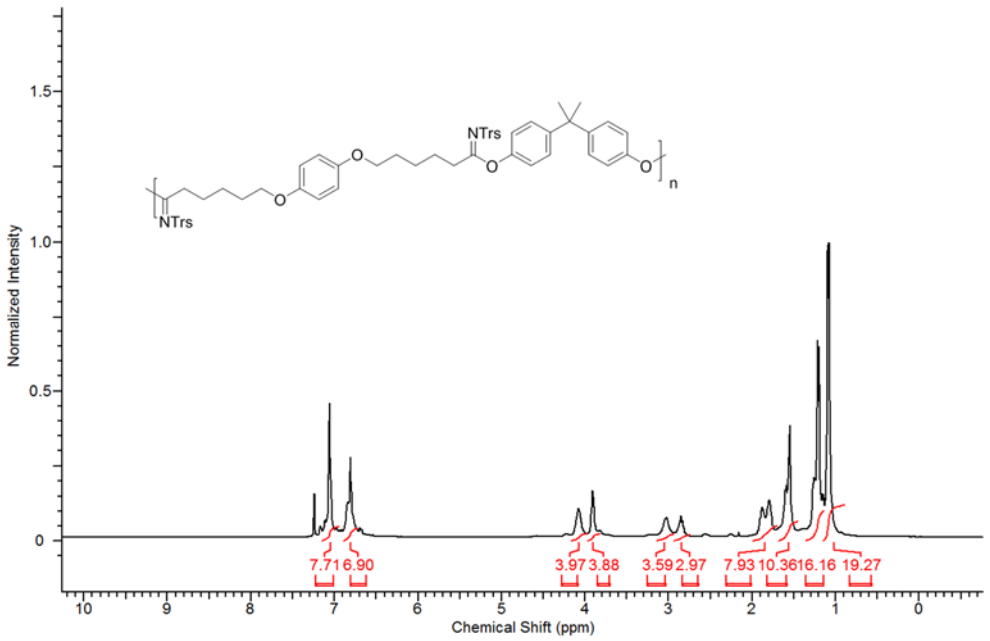


Table Ⅱ－3, entry 23 ($CDCl_3$)



***End-group peak was not observed.**

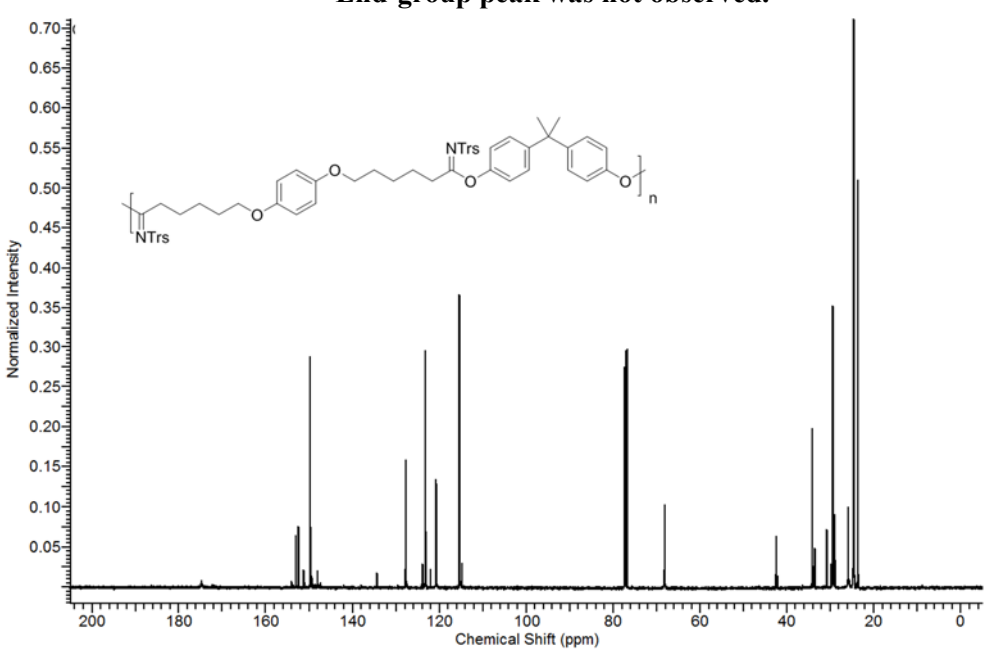
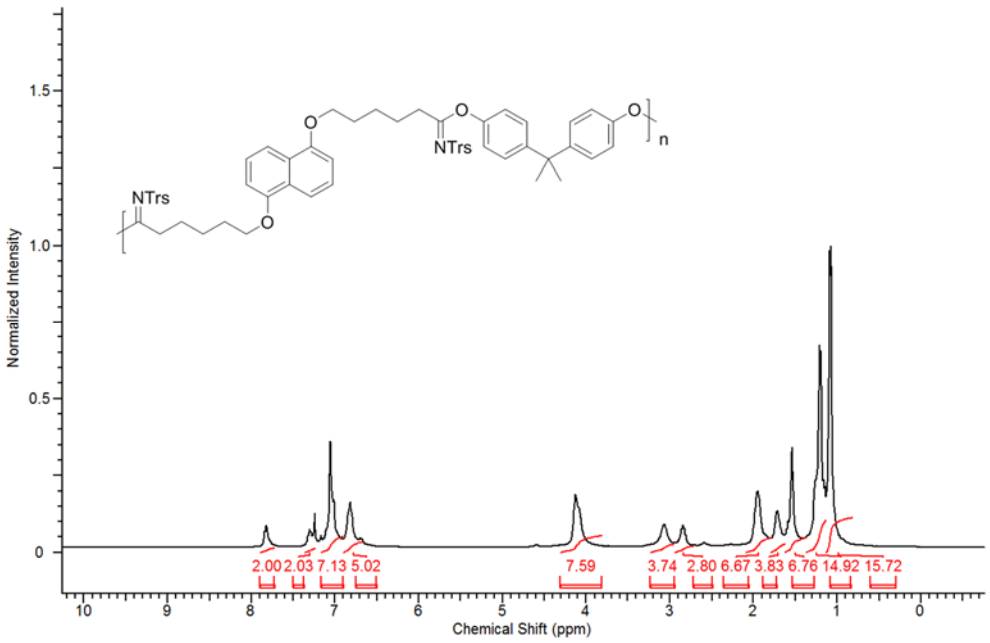
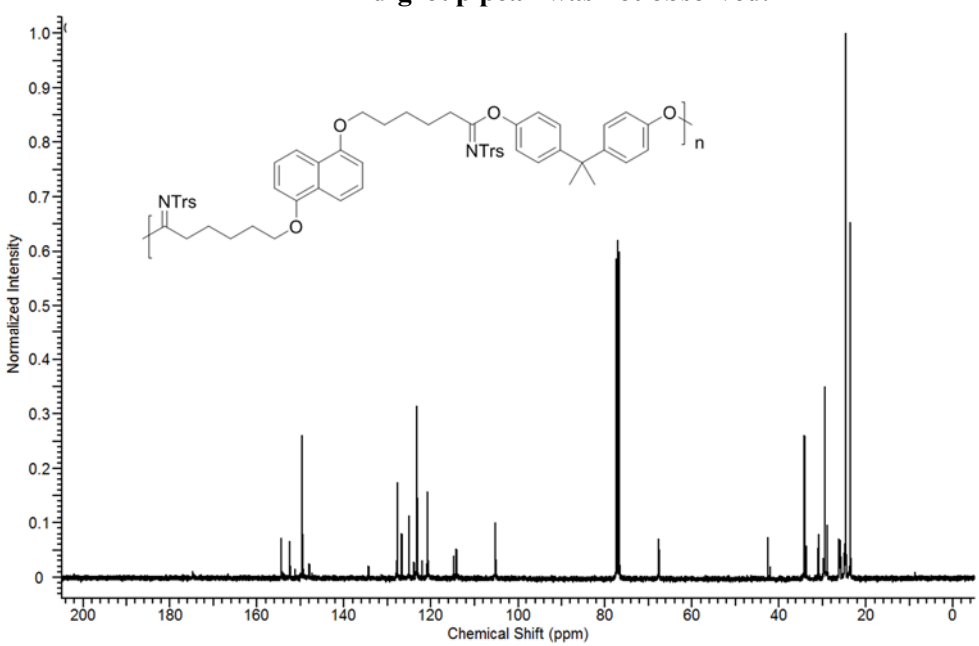


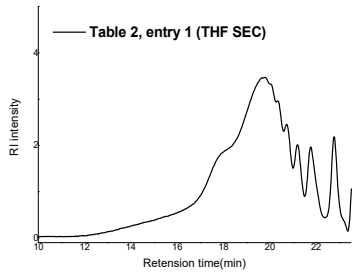
Table Ⅱ－3, entry 24 ($CDCl_3$)

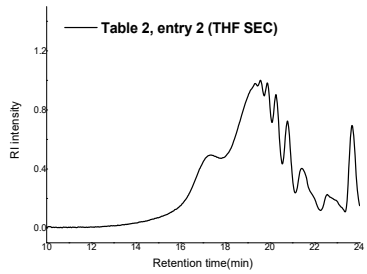


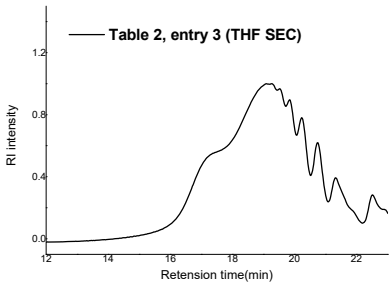
***End-group peak was not observed.**

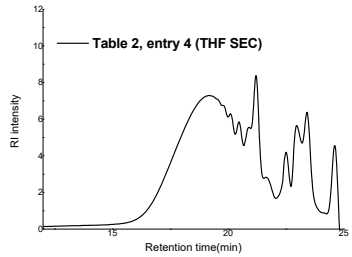


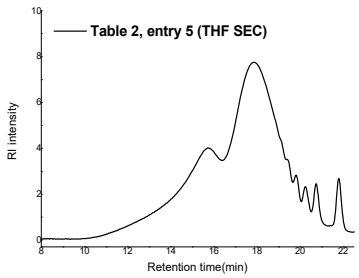
SEC traces of various poly(*N*–sulfonylimidates)

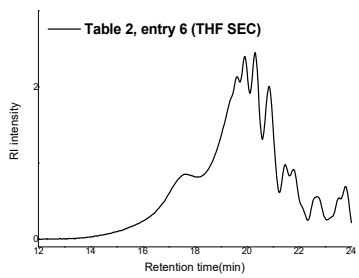


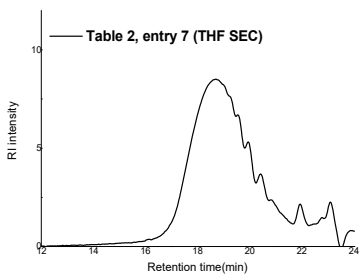


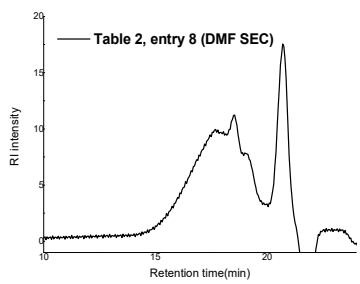












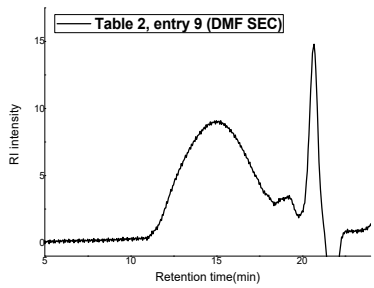


Table 2, entry 9 (DMF SEC)
RI intensity
Retention time(min)

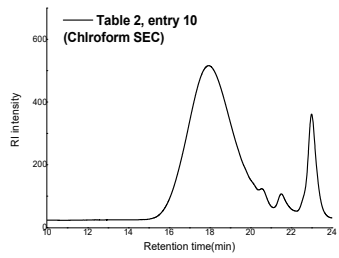


Table 2, entry 10
(Chlroform SEC)
RI intensity
Retention time(min)

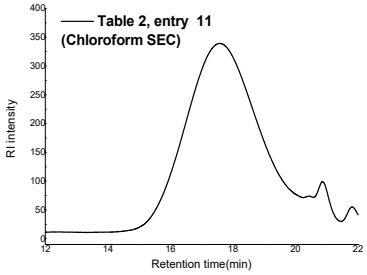


Table 2, entry 11
(Chloroform SEC)
RI intensity
Retention time(min)

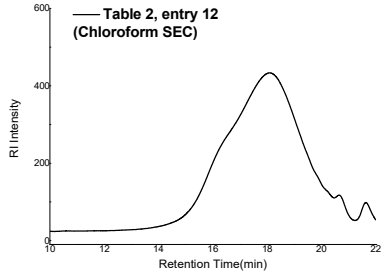


Table 2, entry 12
(Chloroform SEC)
RI Intensity
Retention Time(min)

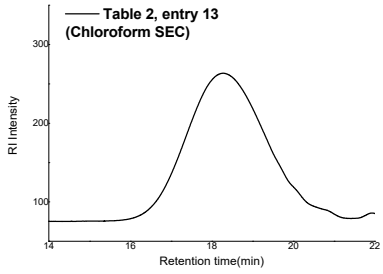


Table 2, entry 13
(Chloroform SEC)
RI Intensity
Retention time(min)

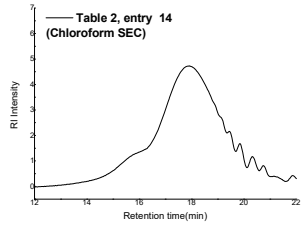


Table 2, entry 14
(Chloroform SEC)
RI Intensity
Retention time(min)

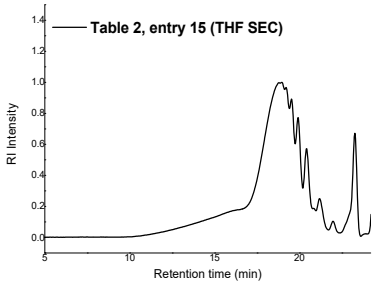


Table 2, entry 15 (THF SEC)
RI Intensity
Retention time (min)

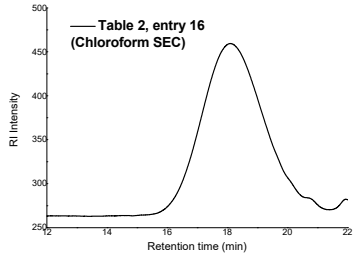


Table 2, entry 16
(Chloroform SEC)
RI Intensity
Retention time (min)

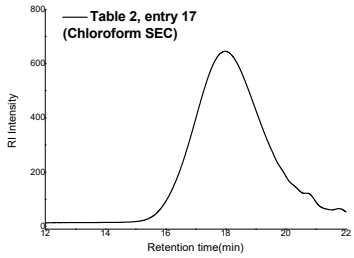


Table 2, entry 17
(Chloroform SEC)
RI Intensity
Retention time(min)

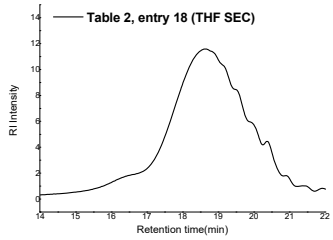


Table 2, entry 18 (THF SEC)
RI Intensity
Retention time(min)

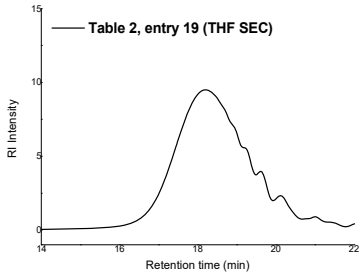


Table 2, entry 19 (THF SEC)
RI Intensity
Retention time (min)

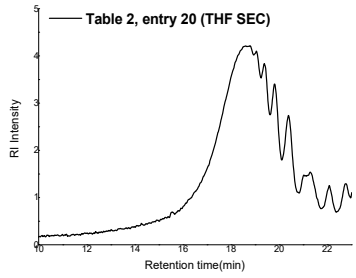


Table 2, entry 20 (THF SEC)
RI Intensity
Retention time(min)

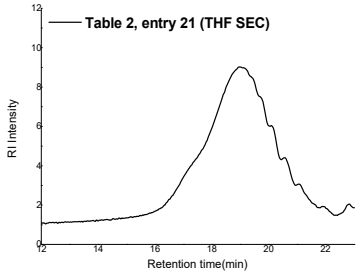


Table 2, entry 21 (THF SEC)
RI Intensity
Retention time(min)

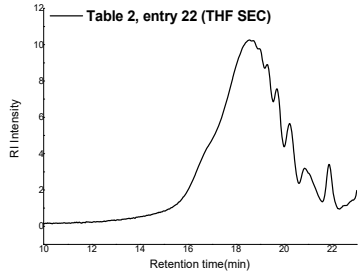


Table 2, entry 22 (THF SEC)
RI Intensity
Retention time(min)

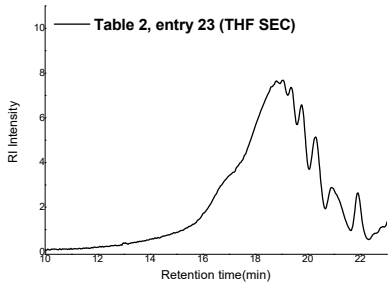


Table 2, entry 23 (THF SEC)
RI Intensity
Retention time(min)

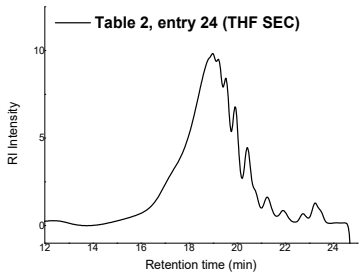
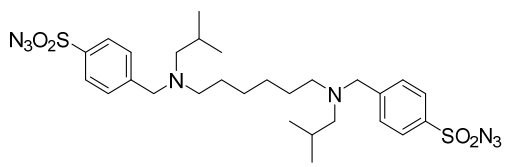


Table 2, entry 24 (THF SEC)
RI Intensity
Retention time (min)

Chapter Ⅲ - Experimental

Synthetic procedure for bis-sulfonyl azide

4,4'-((hexane-1,6-diylbis(isobutylazanediyl))bis(methylene))dibenzenesulfonyl azide (1a)



: To a stirred solution of *N, N*-diisobutylhexane-1,6-diamine (10 mmol, 1.0 eq) and potassium carbonate (30mmol, 3.0eq) in acetonitrile and water mixture (9 : 1), 4-(bromomethyl)benzenesulfonyl chloride (**1**) (22 mmol, 2.2 eq) was added and stirred for 12h at room temperature. After extraction with ethyl acetate twice, the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatograph on silica gel (hexane : EtOAc = 10 : 1), affording 1a as a yellowish viscous liquid (7.3mmol, yield of 73%): ^{1}H NMR (300 MHz, CDCl3) : δ 7.88-7.85 (d, 4H), 7.60-7.58 (d, 4H), 2.36-2.32 (t, 4H), 2.16-2.13 (t, 4H), 1.79-1.70 (m, 2H), 1.42 (br, 4H), 1.24-1.22 (br, 4H), 0.88-0.86 (d, 12H); ^{13}C NMR (75 MHz, CDCl3): δ 149.42, 136.54, 129.62, 127.43, 63.04, 59.04, 54.60, 27.38, 26.58, 20.92; HRMS (FAB^-) : calculated for $C_{28}H_{42}N_8O_4S_2$, 617.2692, observed, 617.2692.

Benzene-1,3-disulfonyl diazide (1b)

: This monomer was prepared by slightly modified method from the previous literature.[2] ^{1}H-NMR, ^{13}C-NMR and MS analysis data are also available in the same literature.

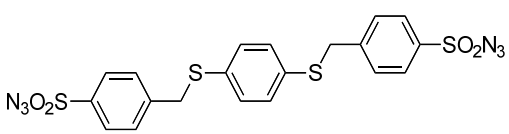
4,4'-oxydibenzenesulfonyl azide (1c)

: This monomer was prepared by the method from the previous literature.[3] ^{1}H-NMR, ^{13}C-NMR and MS analysis data are also available in the same literature.

[1,1'-biphenyl]-4,4'-disulfonyl diazide (1d)

: This monomer was prepared by the method from the previous literature.[4] ^{1}H-NMR, ^{13}C-NMR and MS analysis data are also available in the same literature.

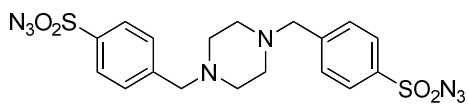
4,4'-((1,4-phenylenebis(sulfanediyl))bis(methylene))dibenzenesulfonyl azide (1e)



: To a stirred solution of benzene-1,4-dithiol (10 mmol, 1.0 eq) and TEA (30mmol, 3.0eq) in THF (30mL), 4-(bromomethyl)benzenesulfonyl chloride (1) (22 mmol, 2.2 eq) was added and stirred for 12h at room temperature. After extraction with dichloromethane twice, the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatograph on silica

gel, affording 1a as a white-yellow solid (6.8mmol, yield of 68%). ^{1}H NMR (300 MHz, DMSO-d_6) : δ 7.96-7.93 (d, 4H), 7.68-7.65 (d, 4H), 7.26(d, 2H), 4.37(s, 4H) ; ^{13}C NMR (75 MHz, DMSO-d_6): δ 146.72, 136.42, 133.54, 130.86, 130.06, 127.95, 36.61; HRMS (FAB^-) : calculated for $C_{20}H_{16}N_6O_4S_4$, 531.0038, observed, 531.0043.

4,4'-(piperazine-1,4-diylbis(methylene))dibenzenesulfonyl azide (1f)

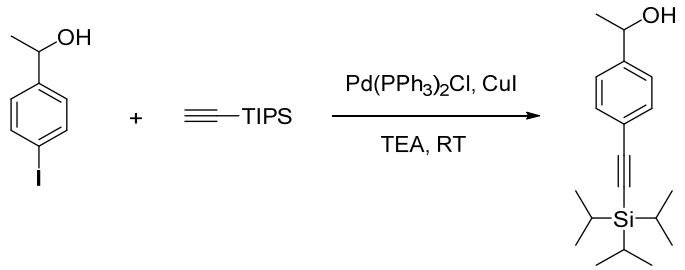


: This monomer was prepared by the same method from the previous bis-sulfonyl azide. (1a) The crude residue was purified by flash column chromatograph on silica gel, affording 1f as a white solid (yield of 76%). ^{1}H NMR (300 MHz, CDCl3) : δ 7.91-7.88 (d, 4H), 7.60-7.57 (d, 4H), 3.61 (s, 4H), 2.51 (s, 8H) ; ^{13}C NMR (75 MHz, CDCl3): δ 146.76, 137.12, 129.98, 127.63, 62.24, 53.25; HRMS (FAB^-) : calculated for $C_{18}H_{20}N_8O_4S_2$, 475.0971 , observed, 475.0974.

Synthesis of mono-functionalized polymer macromonomers

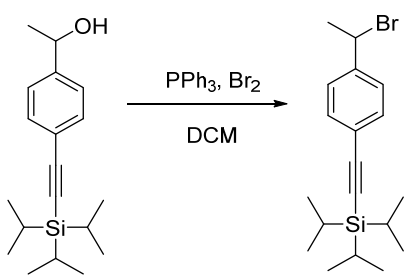
Mono-functionalized Polystyrene

1-(4-((triisopropylsilyl)ethynyl)phenyl)ethan-1-ol (ATRP initiator OH)



: This monomer was prepared by slightly modified method from the previous literature.[5] The product was obtained as tint-peach solid. (98% yield) ^{1}H NMR (300 MHz, CDCl3) : δ 7.46 (d, 2H), 7.30 (d, 2H), 4.92-4.86 (m, 1H), 1.90 (s, 1H), 1.47 (d, 3H), 1.13 (s, 21H), ^{13}C NMR (75 MHz, CDCl3): δ 146.16, 132.31, 125.32, 122.78, 107.06, 90.55, 70.23, 25.32, 18.80, 11.46. HRMS (FAB^{-}) : calculated for $C_{19}H_{30}OSi$, 301.1988 , observed, 301.1992.

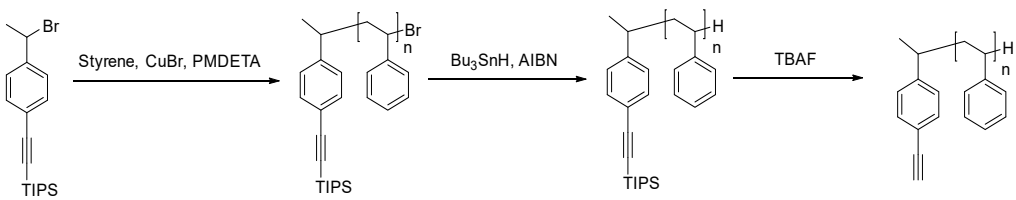
((4-(1-bromoethyl)phenyl)ethynyl)triisopropylsilane (ATRP initiator Br)



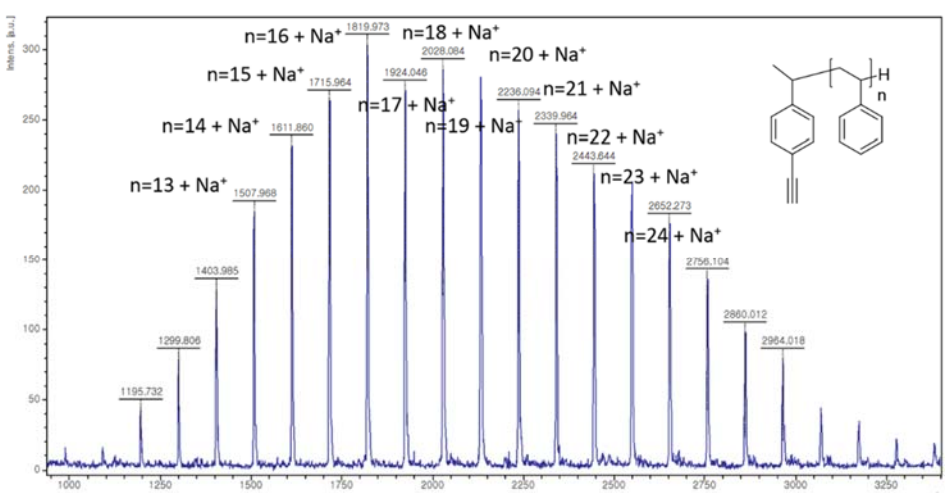
: To a stirred solution of PPh_3 (14.5 mmol) in CH_2Cl_2 (50 mL) at 0° C was added Br_2 (14.5 mmol) dropwise and after 5 min, Et_3N (18.7 mmol) was added and the mixture stirred for a further 5 min. A

solution of the saturated alcohol from above (10 mmol) in CH_2Cl_2 (20 mL) was then added dropwise and the mixture allowed to warm to rt. After 30 min the mixture was concentrated *in vacuo* and purified by flash chromatography to afford the corresponding bromide as a colorless liquid (52% yield).). ^{1}H NMR (300 MHz, CDCl3) : δ 7.47 (d, 2H), 7.38 (d, 2H), 5.30−5.15 (s, t, 1H), 2.05 (d, 3H), 1.16 (s, 21H); ^{13}C NMR (75 MHz, CDCl3): δ 143.39, 132.42, 126.81, 123.71, 106.69, 91.56, 48.84, 26.69, 18.78, 11.43; HRMS (FAB$^-$) : calculated for $C_{24}H_{42}O_4$, 363.1144, observed, 363.1137

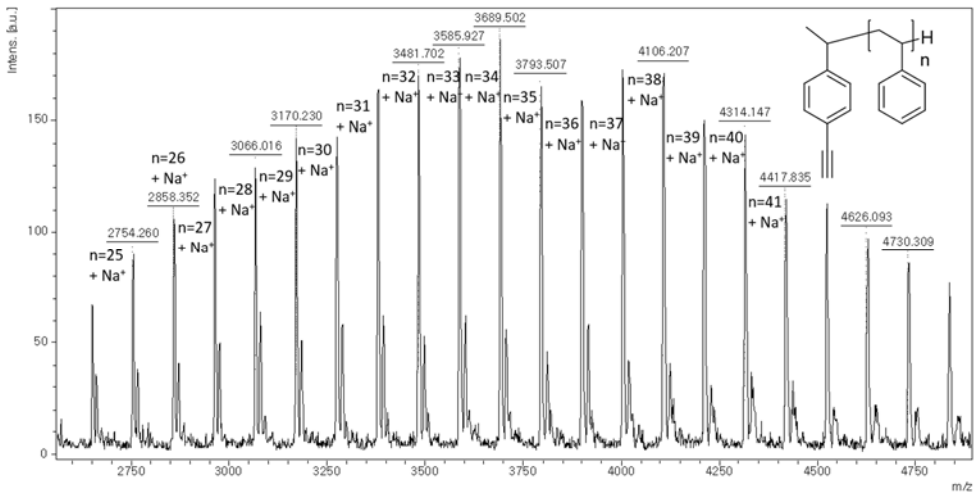
Preparation of mono−functionalized Polystyrene



MALDI−TOF of mono−functionalized PS (M_n=1.8k, PDI=1.04)



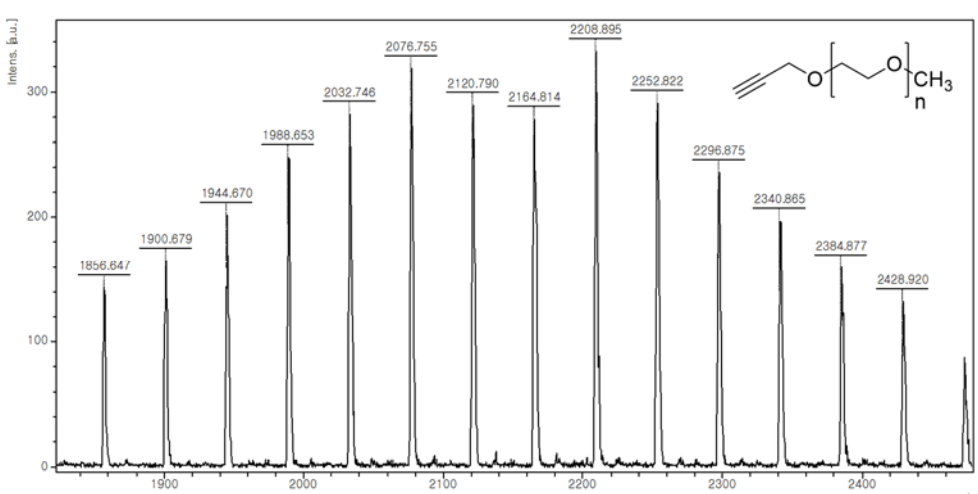
MALDI-TOF of mono-functionalized PS (M_n=3.2k, PDI=1.08)



Mono-functionalized PEG

The procedure for the transformation of mono-functionalized PEG 2k was adapted from the literature.[6]

MALDI-TOF of mono-functionalized PEG (M_n=2.0k)

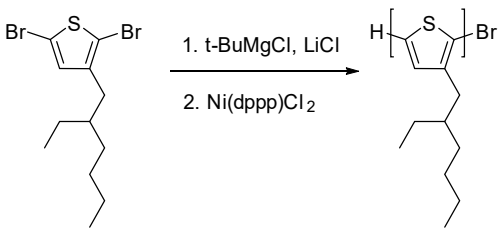


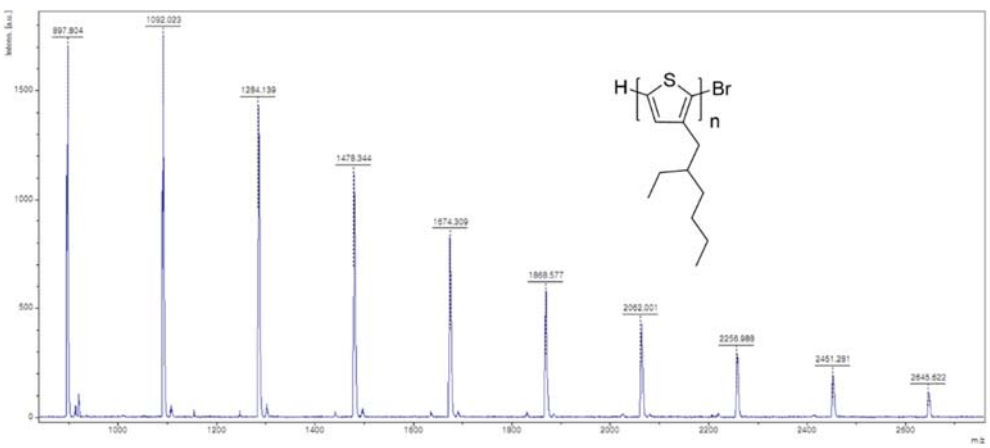
Mono-functionalized P3EHT

Preparation of H/Br ended P3EHT

The procedure for H/Br ended P3EHT was adapted from the literature.[7]

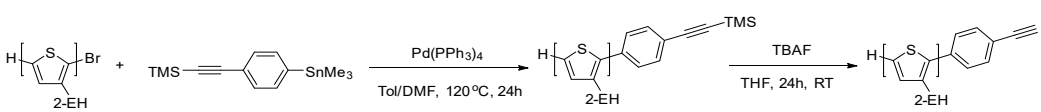
MALDI-TOF of P3EHT (H/Br)

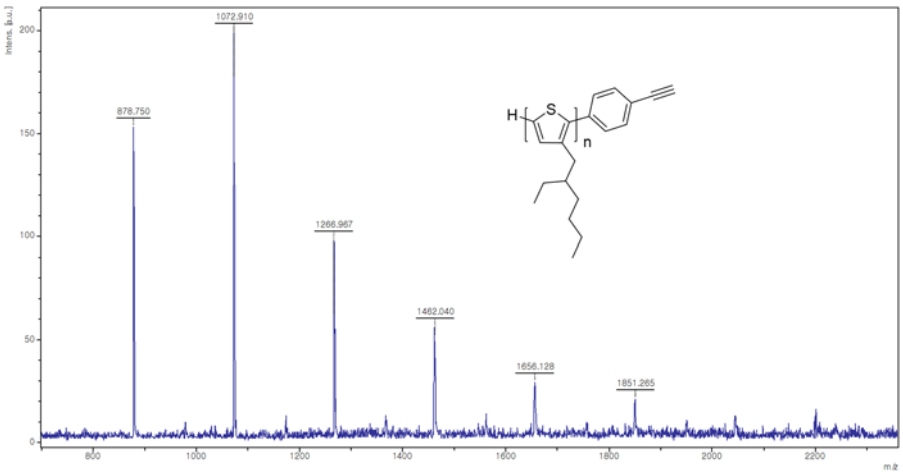




Preparation of mono-functionalized P3EHT

The procedure for the transformation of mono-functionalized P3EHT was adapted from the literature.[8]





General procedure for mono-functionalized dendronized macromonomers

: To a stirred solution of dendron-OH (2 mmol, 1.0 eq) in THF (20mL), sodium hydride (60wt% dispersion in mineral oil) (10mmol, 5.0eq) and 15-crown-5 (0.5 eq) was added slowly at 0°C and stirred for 20min under Ar condition. To a reaction mixture, propagyl bromide (80wt% in toluene) and stirred for 18h at 70°C. The reaction was quenched by water at 0°C. After extraction with dichloromethane twice, the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatograph on silica gel to afford a corresponding dendronized macromonomer.

1) Fréchet Dendron 2nd and 3rd generation

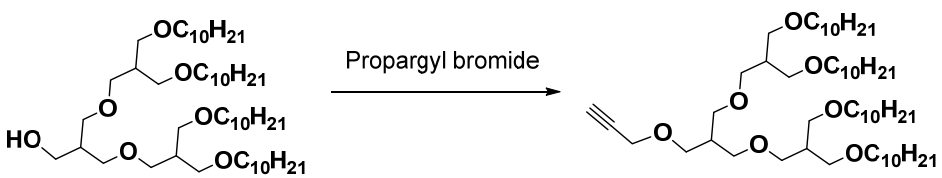
: This monomer was prepared by the method from the previous literature.[1]H-NMR, [13]C-NMR and MS analysis data are also available in the same literature.[9]

2) Ester Dendron 2nd and 3rd generation

: This monomer was prepared by the method from the previous literature. [1]H-NMR, [13]C-NMR and MS analysis data are also available in the same literature.[10]

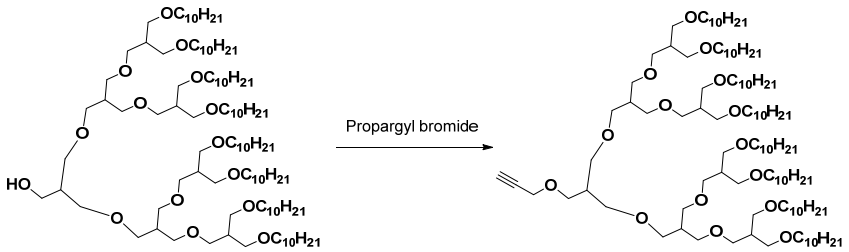
3) Ether Dendron 2nd and 3rd generation

Preparation of mono-functionalized Ether G2 dendron



Ether G2 dendron was prepared from Ether G2-OH[11] following general procedure (eluent: hexanes/ethyl acetate = 5/1). The product was obtained as colorless oil (81% yield). [1]H-NMR (300MHz, $CDCl_3$): δ 4.11 (d, 2H), 3.54 (d, 2H), 3.43 (m, 8H), 3.42 (d, 8H) 3.37 (t, 8H), 2.39 (t, 1H), 2.13 (m, 3H), 1.54 (pent, 8H), 1.28 (m, 56H), 0.87 (t, 12H). [13]C-NMR (75MHz, $CDCl_3$): δ 80.10, 74.19, 71.41, 69.46, 69.31, 68.75, 58.47, 40.45, 40.30, 32.03, 29.82, 29.77, 29.73, 29.46, 26.33, 22.80, 14.23. MALDI-TOF calculated for $C_{55}H_{108}O_4$, 881.46, observed, 882.267

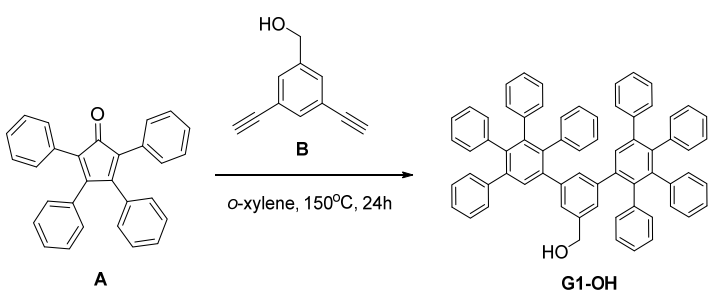
Preparation of mono-functionalized Ether G3 dendron



Ether G3 dendron was prepared from Ether G3-OH[11, 12] following general procedure (eluent: hexanes/ethyl acetate = 5/1). The product was obtained as colorless oil (78% yield). ^{1}H-NMR (300MHz, $CDCl_3$): δ 4.10 (d, 2H), 3.55 (d, 2H), 3.42-3.44 (m, 70H), 2.43 (t, 1H), 2.11 (pent, 9H), 1.53 (pent, 21H), 1.25 (m, 140H), 0.87 (t, 28H). ^{13}C-NMR (75MHz, $CDCl_3$): δ 80.09, 74.40, 71.41, 69.81, 69.75, 69.63, 69.56, 69.32, 68.53, 58.47, 40.46, 40.40, 40.34, 32.05, 29.84, 29.79, 29.66, 29.49, 26.33, 22.81, 14.24. MALDI-TOF [M+Na^+] calculated for $C_{111}H_{220}O_{15}$, 1817.96, observed, 1817.543.

4) Müllen Dendron 1st and 2nd generation

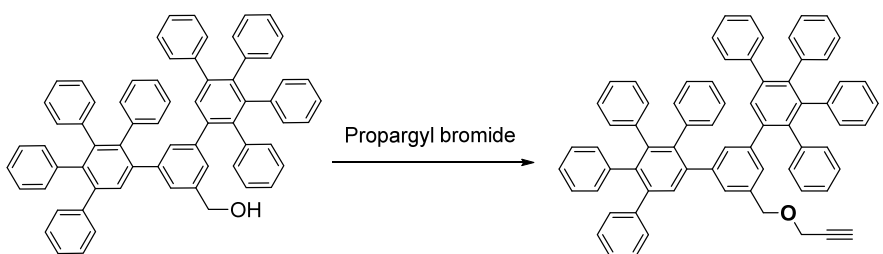
Preparation of Müllen G1-OH[13]



A (10 mmol, 2.5 eq) and B (4 mmol, 1.0 eq) in 20ml of *o*-xylene

were stirred for 24h at 150°C under an argon atmosphere. Solvent was removed under reduced pressure and the crude product was purified by flash column chromatograph on silica gel (dichloromethane). The product was obtained as a white solid (89% yield). ^{1}H-NMR (300MHz, CD_2Cl_2): δ 7.30-7.27 (s, 2H), 7.21-7.10 (m, 10H), 7.09-7.06 (s, 1H), 7.00-6.69 (m, 32H), 4.36, 4.19 (d, 2H) ; ^{13}C-NMR (75MHz, CD_2Cl_2): δ 141.70, 141.52, 140.94, 140.38, 140.29, 140.23, 140.05, 139.61, 139.41, 139.29, 131.80, 131.58, 131.29, 130.13, 127.61, 127.13, 127.01, 126.91, 126.73, 125.70, 125.45, 65.37. MALDI-TOF calculated for $C_{67}H_{48}O$, 869.12, observed, 868.783.

Preparation of mono-functionalized Müllen G1 dendron

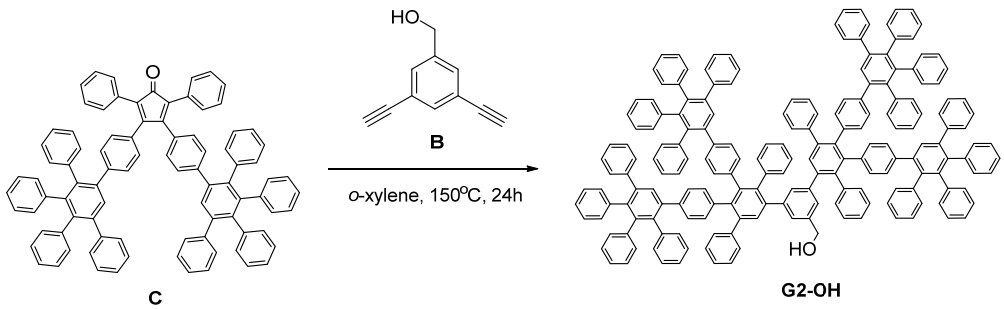


G1-OH

Müllen G1 dendron was prepared from G1-OH[13] following general procedure (eluent: hexanes/dichloromethane = 1/1). The product was obtained as a white solid (88% yield). ^{1}H-NMR (300MHz, CD_2Cl_2): δ 7.35-7.26(s, 1H), 7.24-7.09(m, 12H), 7.07-6.98(s, 2H), 6.96-6.72(m, 30H), 4.28-4.16(s, 2H), 3.64-3.48(d, 2H), 2.43-2.34(t, 1H) ; ^{13}C-NMR (75MHz, CD_2Cl_2): δ 141.71, 141.32, 140.78, 140.43, 140.10, 140.03, 139.30, 139.17, 135.86, 131.52, 131.46, 131.41, 131.12, 129.94, 128.00, 127.44, 126.92, 126.76,

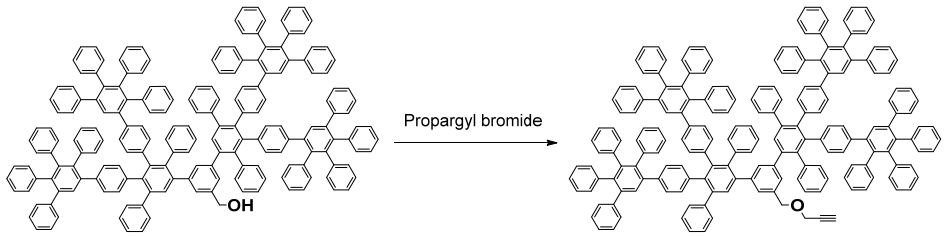
126.47, 126.22, 125.73, 125.53, 125.25, 80.01, 73.92, 70.82, 56.10. MALDI-TOF calculated for $C_{70}H_{50}O$, 907.17, observed, 906.740.

Preparation of Müllen G2-OH



C[13] (10 mmol, 2.5 eq) and B[14] (4 mmol, 1.0 eq) in 20ml of *o*-xylene were stirred for 48h at 200°C under an argon atmosphere. Solvent was removed under reduced pressure and the crude product was purified by flash column chromatograph on silica gel (hexanes/dichloromethane = 1/1). The product was obtained as a bright yellow solid (81% yield). ^{1}H-NMR (500MHz, CD_2Cl_2): δ 7.46-7.40 (s, 2H), 7.40-7.35 (s, 2H), 7.23-7.14 (m, 28H), 7.08-7.04 (m, 4H), 6.95-6.86 (m, 51H), 6.83-6.76 (m, 14H), 6.76-6.71 (m, 8H), 6.71-6.68 (m, 4H), 6.68-6.64 (d, 4H), 6.57-6.53 (d, 4H), 6.50-6.46 (d, 4H), 4.28-4.22 (d, 2H) ; ^{13}C-NMR (75MHz, CD_2Cl_2): δ 141.87, 141.69, 140.69, 140.60, 140.21, 140.09, 140.01, 139.21, 139.17, 139.12, 138.82, 138.43, 138.16, 131.70, 131.50, 131.30, 131.04, 130.98, 130.91, 130.00, 129.89, 128.57, 128.29, 127.49, 126.94, 126.78, 126.75, 126.45, 126.18, 125.69, 125.51, 125.23, 64.78. MALDI-TOF calculated for $C_{187}H_{128}O$, 2391.08, observed, 2390.590.

Preparation of mono-functionalized Müllen G2 dendron

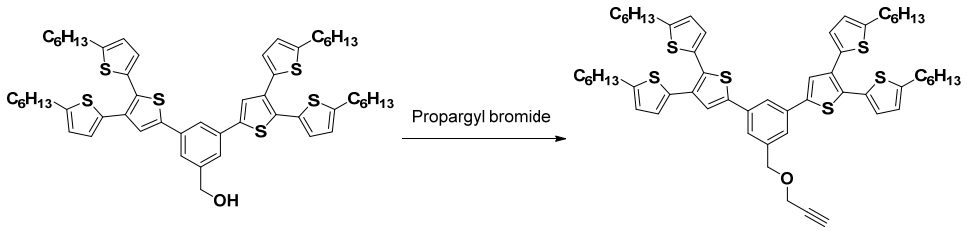


G2-OH

Müllen G2 dendron was prepared from G2-OH following general procedure (hexanes/dichloromethane = 1/1). The product was obtained as a white solid (82% yield). ^{1}H-NMR (500MHz, CD_2Cl_2): δ 7.47-7.39 (s, 2H), 7.39-7.37 (s, 2H), 7.24-7.13(m, 28H), 7.09-7.04 (m, 4H), 6.98-6.85 (m, 51H), 6.83-6.77 (m, 14H), 6.77-6.72(m, 8H), 6.72-6.68 (m, 4H), 6.68-6.63 (d, 4H), 6.58-6.53 (d, 4H), 6.50-6.43 (d, 4H), 4.26-4.17 (s, 2H), 3.63-3.53 (d, 2H), 2.45-2.37 (t, 1H) ; ^{13}C-NMR (75MHz, CD_2Cl_2): δ 141.95, 141.81, 140.87, 140.81, 140.69, 140.56, 140.48, 140.36, 140.30, 140.11, 139.30, 139.23, 139.16, 138.91, 138.88, 131.74, 131.59, 131.17, 131.10, 129.99, 128.70, 128.41, 127.61, 127.10, 126.89, 126.58, 126.30, 125.64, 125.36, 80.00, 74.11, 70.96, 56.17. MALDI-TOF calculated for $C_{190}H_{130}O$, 2429.13, observed, 2429.764.

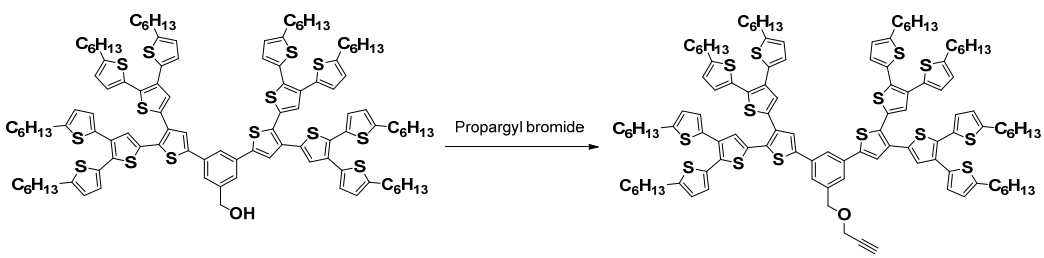
5) Thiophene Dendron 2nd and 3rd generation

Preparation of mono-functionalized Thiophene G2 dendron



Thiophene G2 dendron was prepared from G2-OH[15] following general procedure (hexanes/ethyl acetate = 40/1). The product was obtained as a brown oil (83% yield). 1H NMR (300 MHz, CDCl3): δ 7.75 (s, 1H), 7.53 (s, 2H), 7.40 (s, 2H), 7.01-6.95 (two dd, d, 4H), 6.71(s, 4H), 4.69 (s, 2H), 4.28 (s, 2H), 2.85-2.78 (t, 8H), 2.54-2.52(t, 1H), 1.73-1.64 (t, 8H), 1.36 (m, 24H), 0.93 (s, 12H), ^{13}C-NMR (75MHz, $CDCl_3$): δ 147.62, 146.38, 140.98, 139.07, 134.78, 132.66, 132.41, 131.74, 127.47, 126.48, 124.34, 122.16, 79.55, 75.10, 71.17, 57.49, 53.54, 31.67, 30.27, 28.87, 22.71, 14.21. MALDI-TOF calculated for $C_{58}H_{70}OS_6$, 975.56, observed, 974.398.

Preparation of mono-functionalized Thiophene G3 dendron



Thiophene G3 dendron was prepared from G3-OH[15] following general procedure (hexanes/ethyl acetate = 35/1). The product was obtained as a dark brown oil (82% yield). ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.90-7.75 (s, 1H), 7.69-7.54 (s, 2H), 7.56-7.43 (s, 2H), 7.43-

7.25 (d, 4H), 7.10−6.88 (m, 8H), 6.88−6.57 (s, 8H), 4.80−4.66 (s, 2H), 4.41−4.30 (d, 2H), 2.99−2.69 (m, 16H), 2.62−2.50 (t, 1H), 1.86−1.60 (m, 16H), 1.60−1.16 (m, 48H), 1.16−.067 (t, 24H) ; ^{13}C−NMR (75MHz, $CDCl_3$): δ 147.69, 147.48, 146.33, 146.17, 141.90, 139.33, 134.91, 134.87, 134.53, 132.99, 132.63, 132.60, 132.01, 131.97, 131.32, 130.31, 129.81, 127.67, 127.57, 126.48, 126.33, 124.57, 124.25, 124.22, 124.09, 122.24, 57.58, 53.48, 31.66, 31.57, 30.25, 30.22, 28.87, 28.85, 22.68, 14.17. MALDI−TOF calculated for $C_{114}H_{134}OS_{14}$, 1969.17, observed, 1969.018.

Experimental Supports – references

(1) Hu, X.; Sun, J.; Wang, H.−G.; Manetsch, R. *J. Am. Chem. Soc.*, 2008, *130*, 13820−13821.

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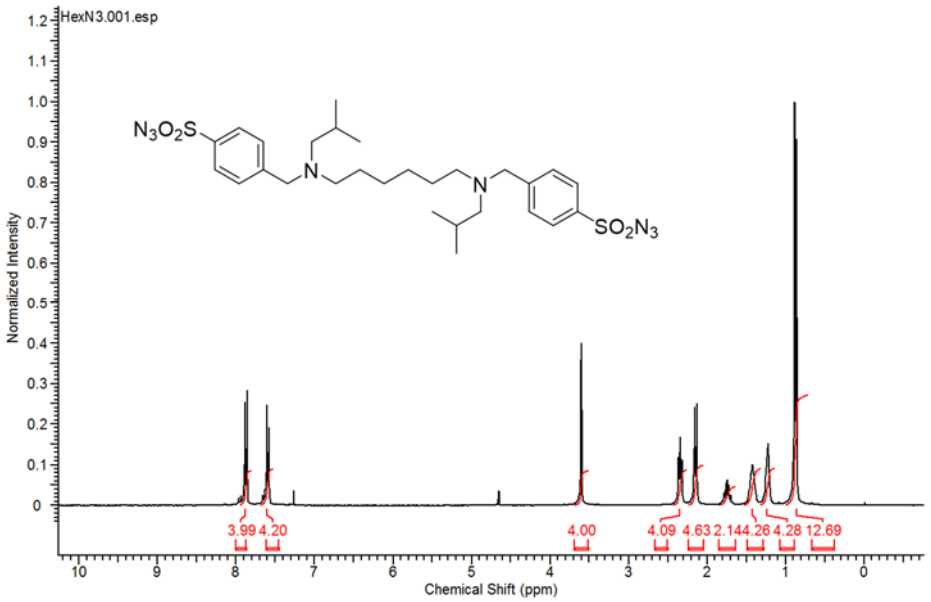
General polymerization procedure

: Mono-functionalized macromonomer (3 eq), Bis-sulfonyl azide (1 eq), Diamine/Diol (1 eq) and 10 mol% of $Cu(ACN)_4PF_6$ was added to reaction flask and purged with Ar atmosphere 3 times. And then degassed toluene/DMF (1/1) mixture (**1M to bis-sulfonyl azide or diamine/diol**) and TOA or TEA (5 eq) was added. The polymerization underwent at 110°C for 18 h under Ar atmosphere. The resulting mixture was precipitated into selected solvent. (PS graft polymer-acetone/methanol (3/1), PEG graft polymer-dichloromethane/ether (3/1), P3EHT graft polymer-dichloromethane/methanol (3/1), Fréchet dendronized polymer-acetone, Müllen dendronized polymer-diethyl ether/dichloromethane (9/1), ether dendronized polymer-acetone, ester dendronized polymer-methanol, thiophene dendronized polymer-methanol). The resulting polymers were dissolved in $CHCl_3$ and passed through the short neutral alumina column to remove the residual copper. Then, those were precipitated again into selected solvent to ensure complete removal of monomers, and dried under vacuum, which afforded pale brown solid (Table Ⅲ-2, entries 1-12), dark brown solid (Table Ⅲ-2, entries 13-16), dark red solid (Table Ⅲ-2, entries 17 and 18), pale or dark brown solid solid (Table Ⅲ-4, entries 1-23), dark brown sticky solid (Table Ⅲ-4, entries 24-29), light green solid (Table Ⅲ-4, entries 30-32) and sticky brown-green solid (Table Ⅲ-4, entries 33-36).

^{1}H NMR and ^{13}C NMR spectra of monomers

Table Ⅲ-2, 1a ($CDCl_3$)



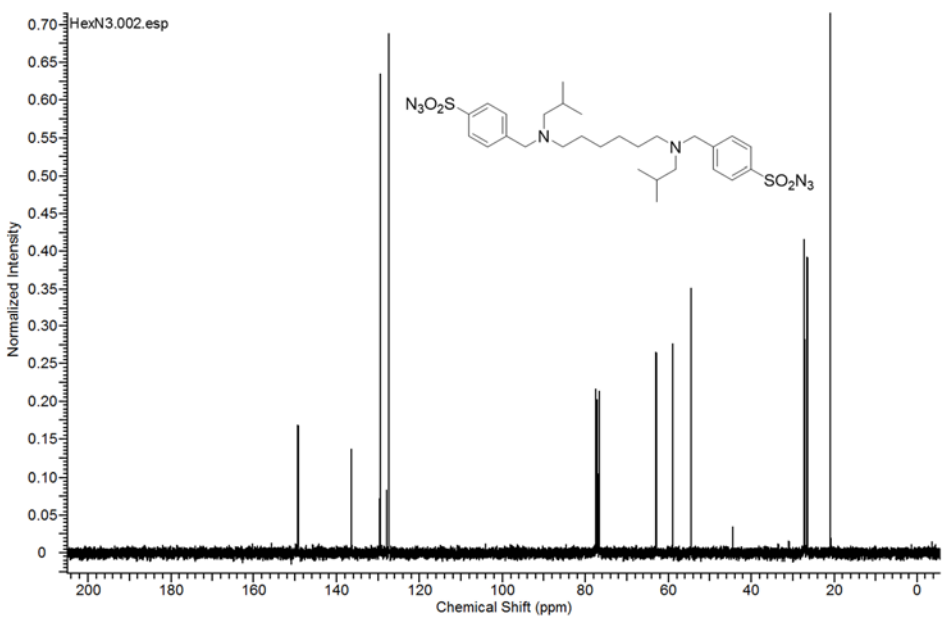
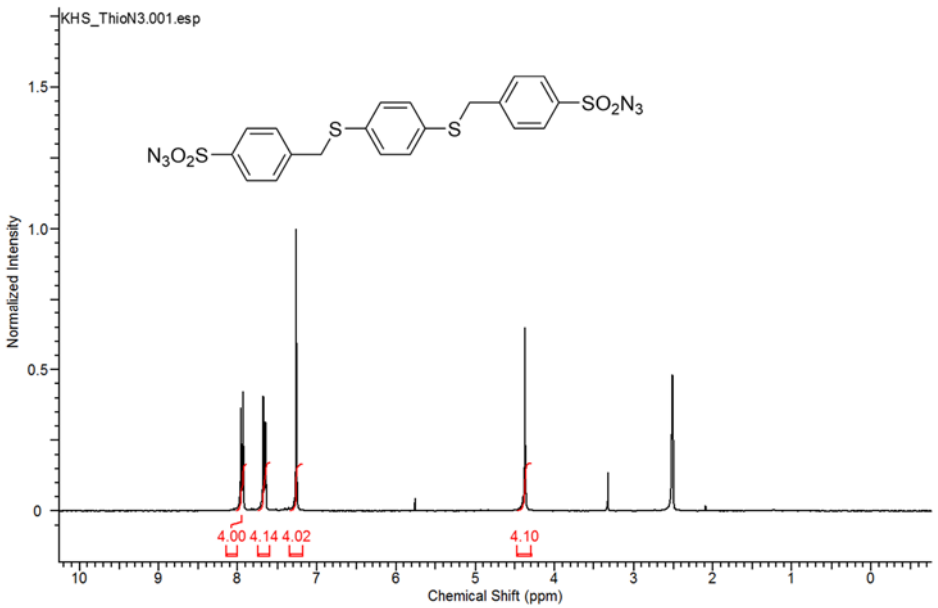


Table Ⅲ-2, 1e (DMSO-d_6)



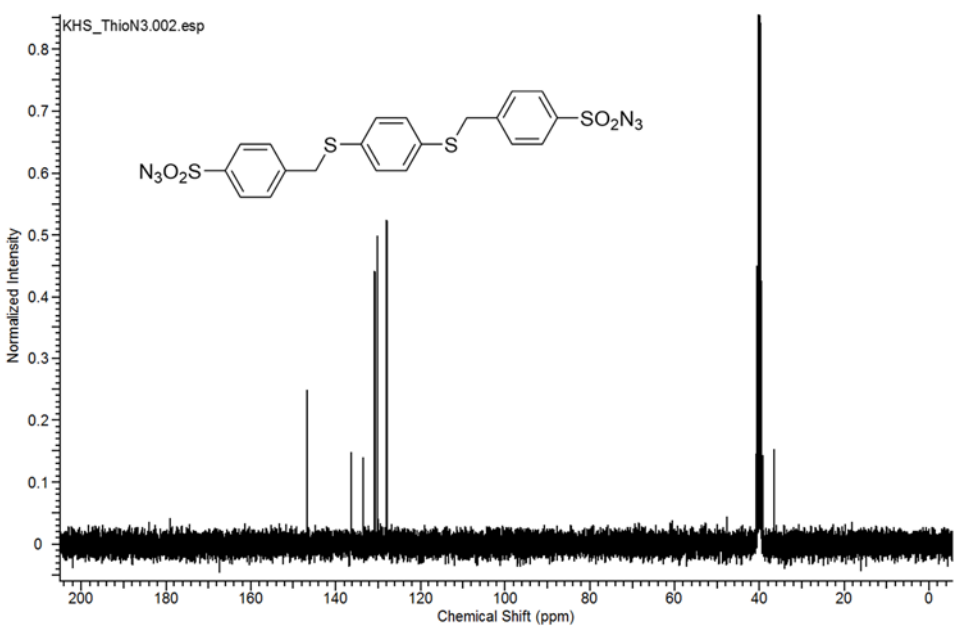
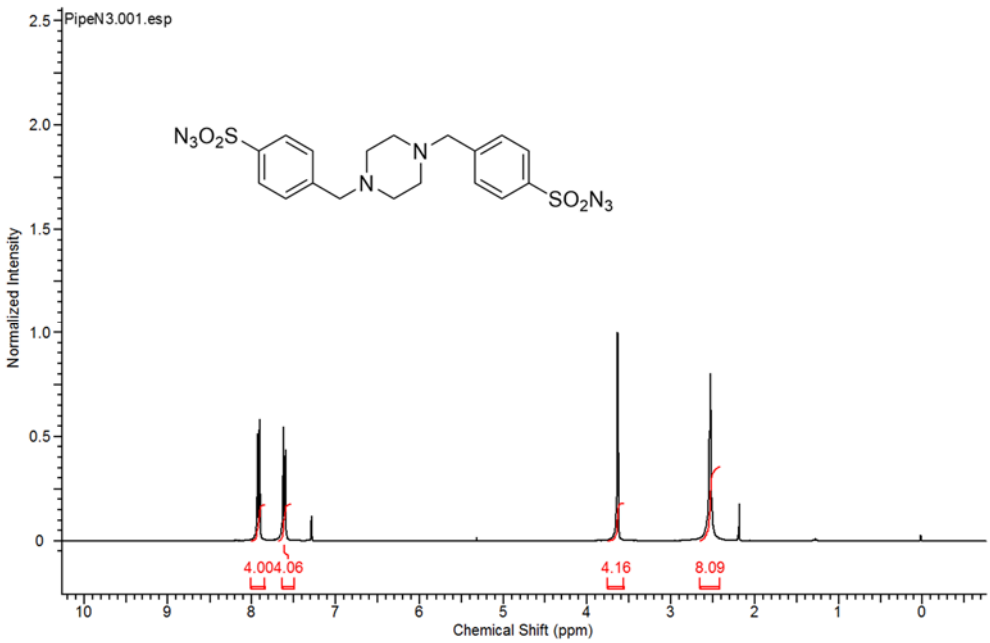
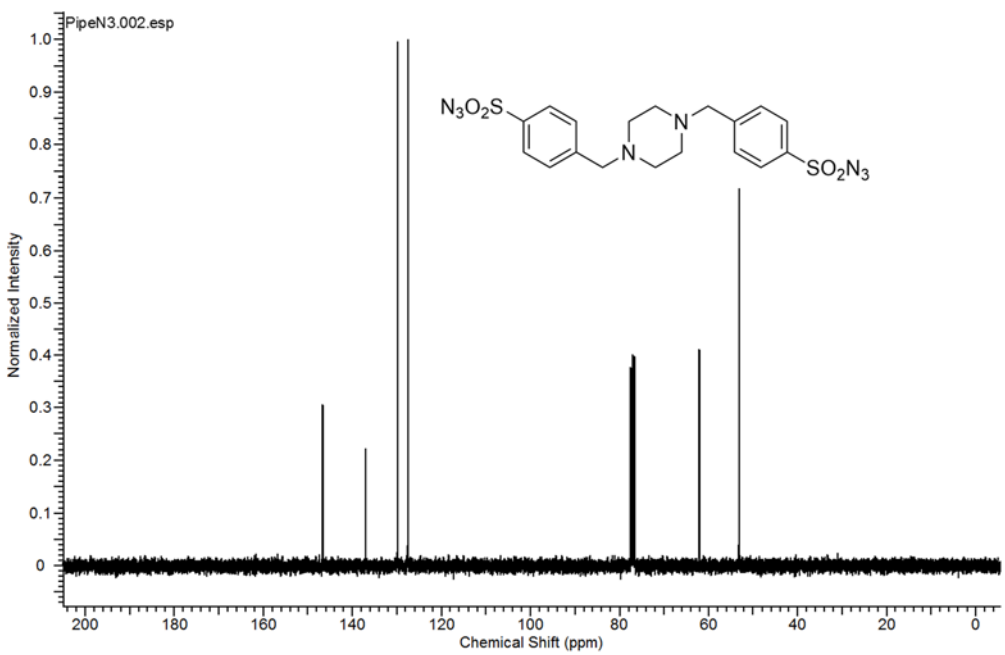
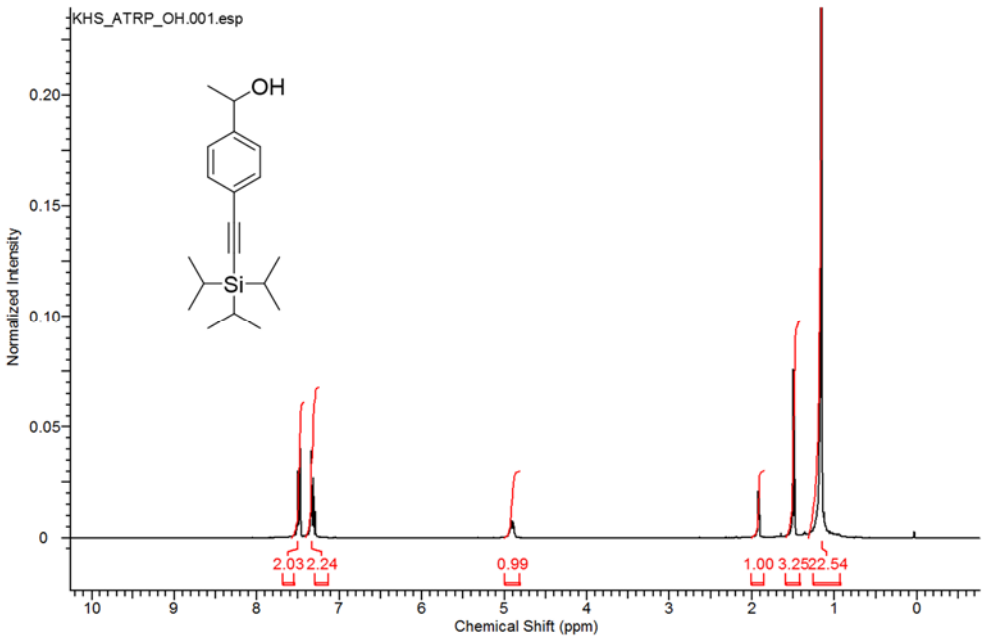


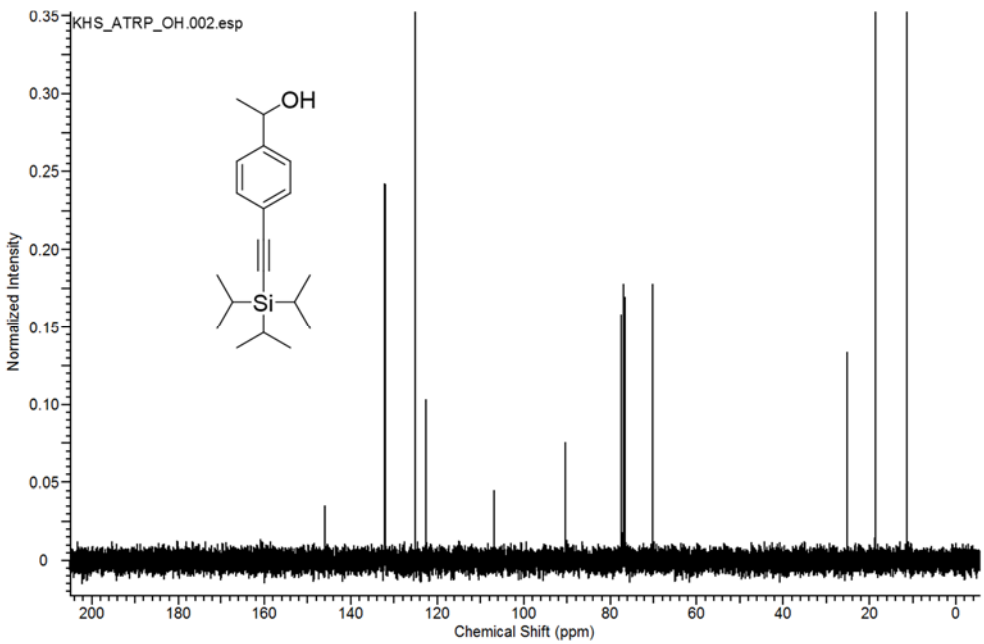
Table Ⅲ-4, 1f ($CDCl_3$)



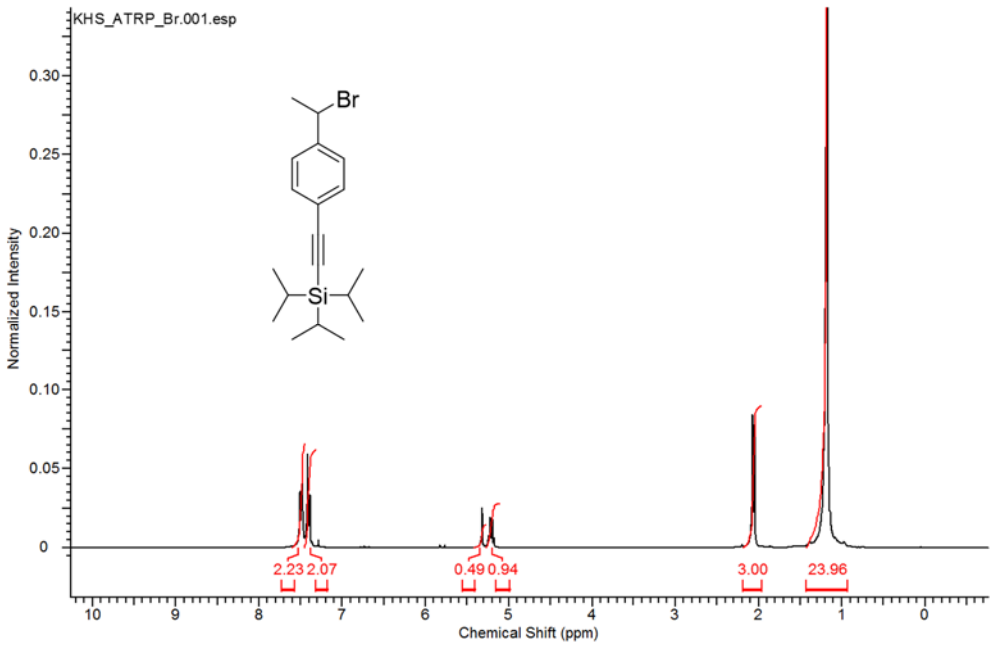


ATRP initiator-OH ($CDCl_3$)





ATRP initiator-Br ($CDCl_3$)



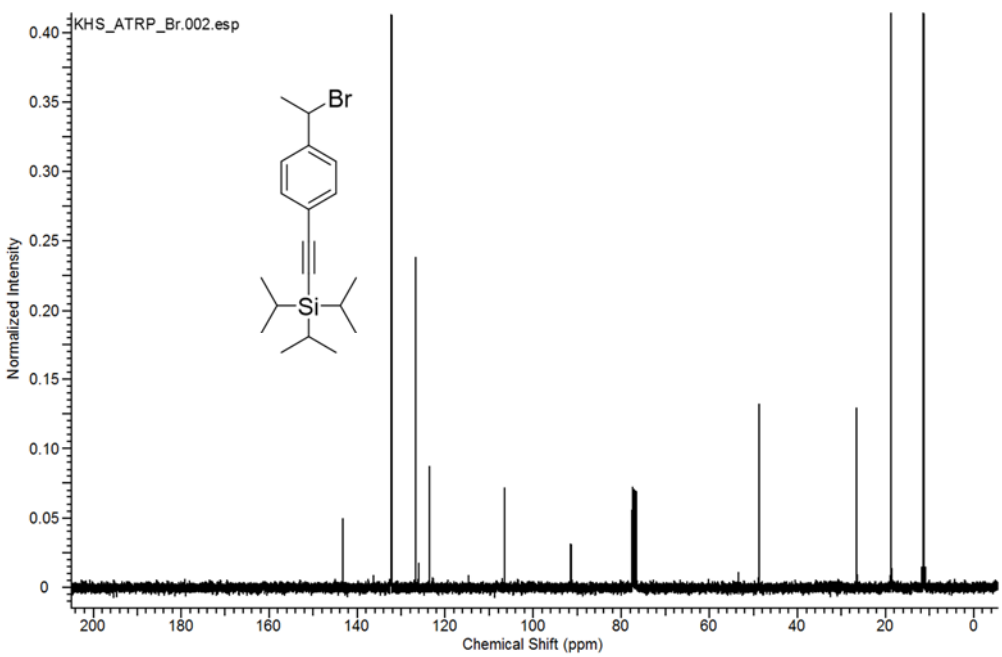


Figure Ⅲ-7, Ether G2 dendron ($CDCl_3$)

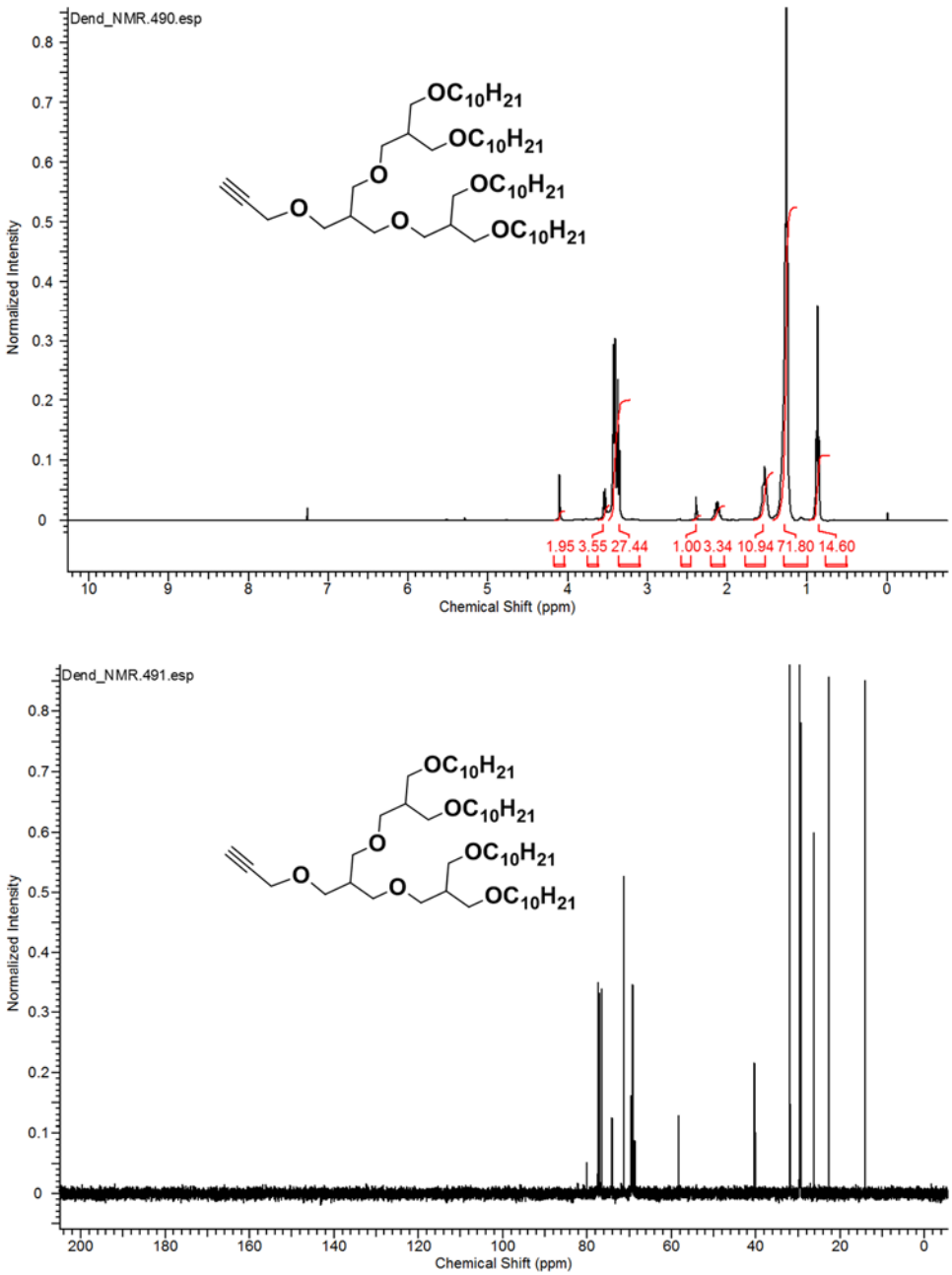
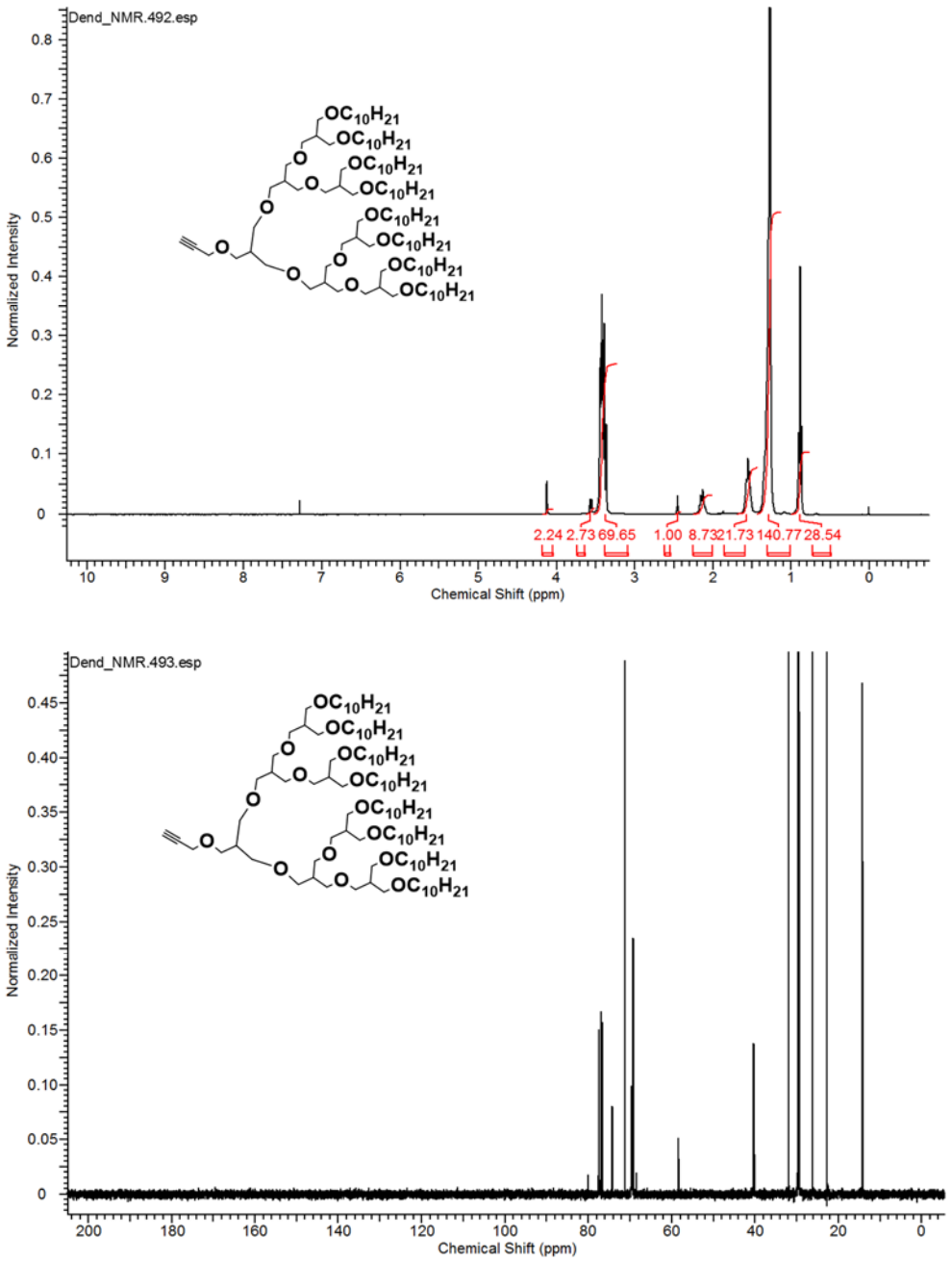
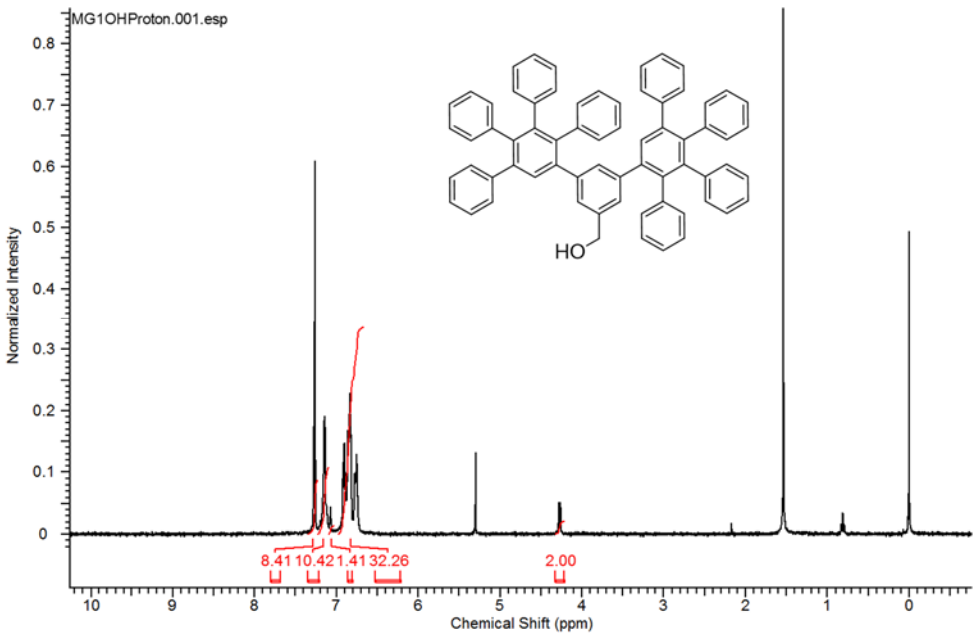


Figure Ⅲ-7, Ether G3 dendron ($CDCl_3$)



Müllen G1-OH (CD_2Cl_2)



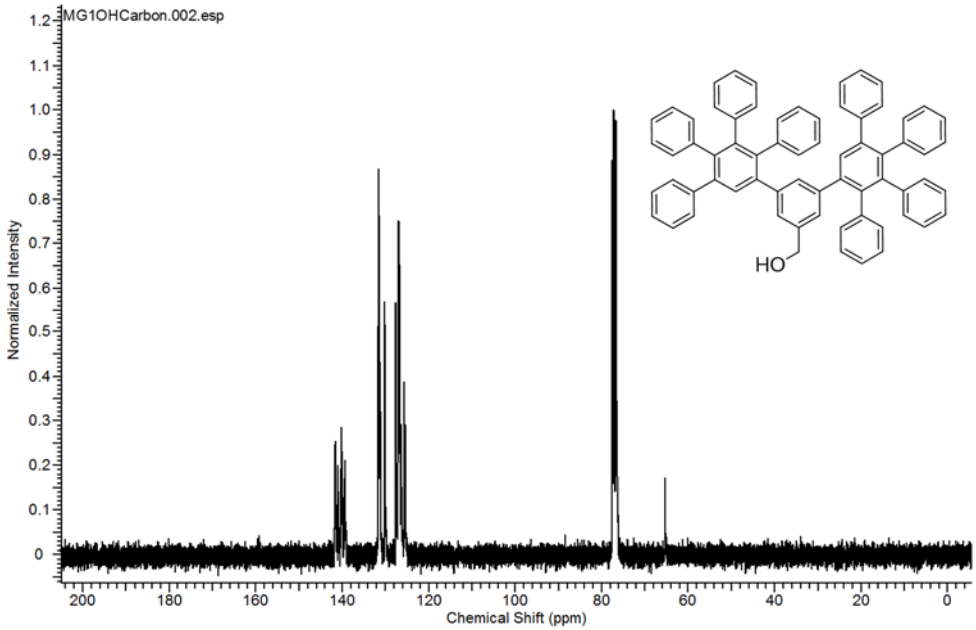
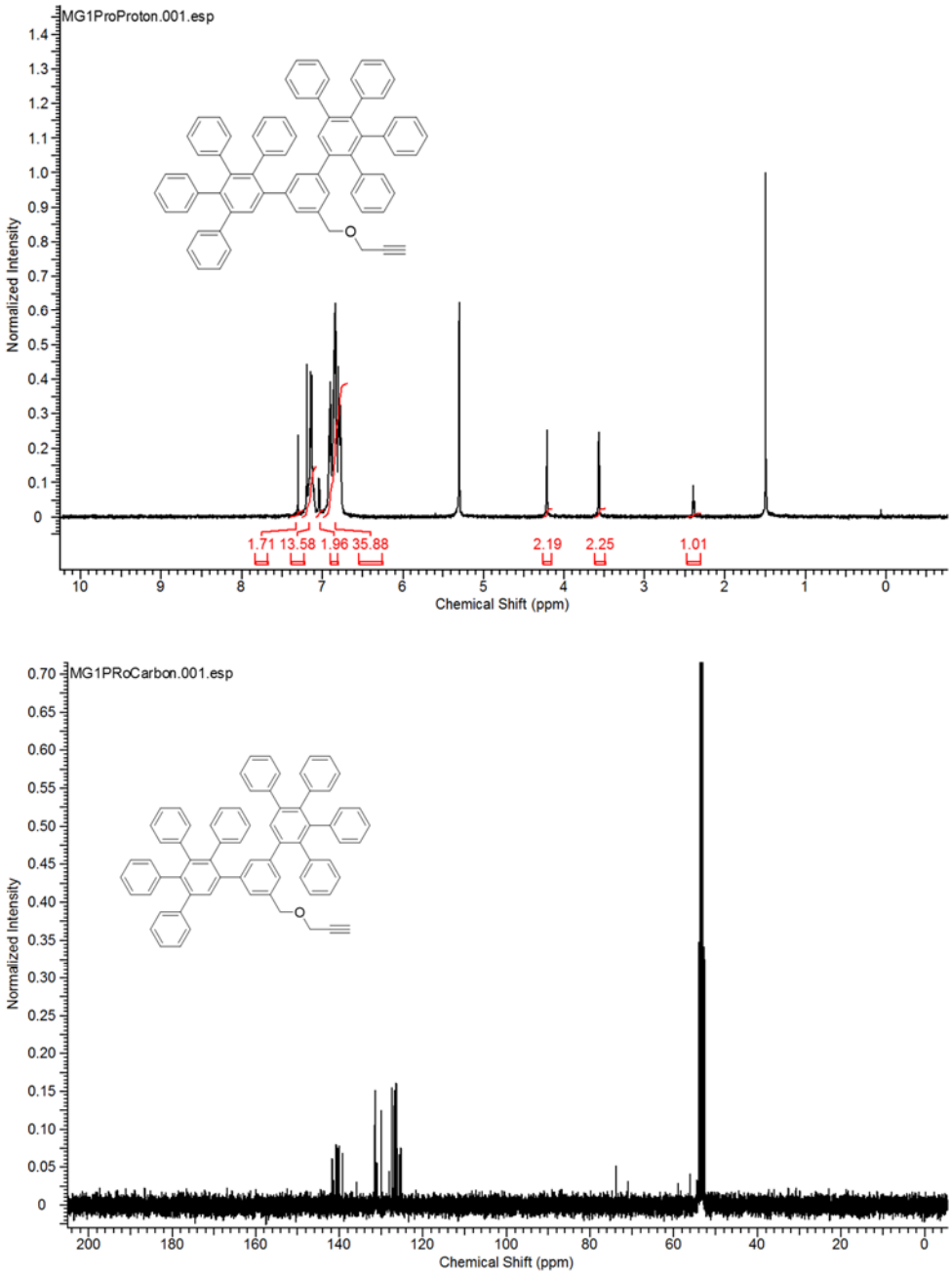
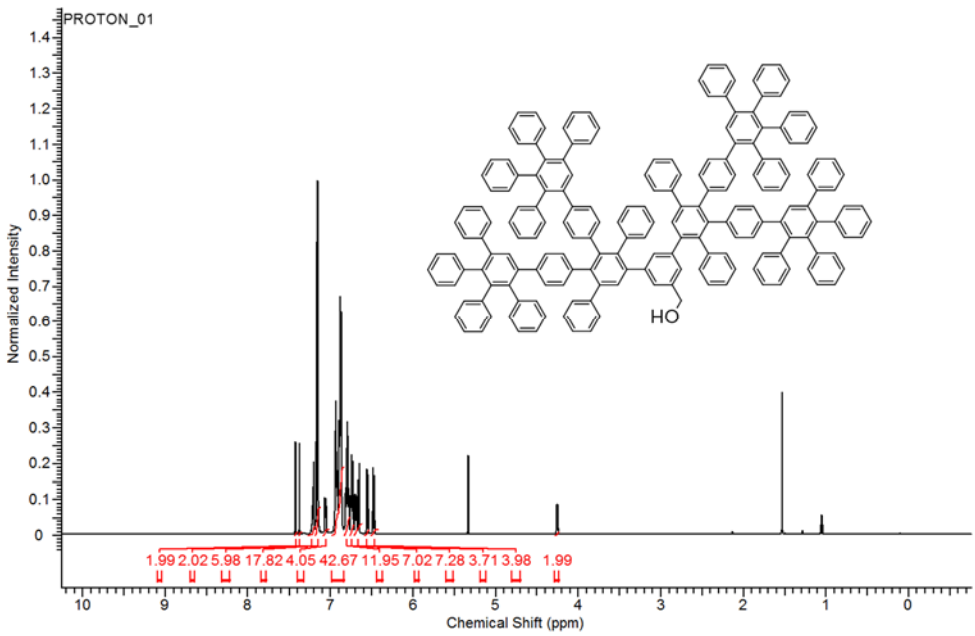


Figure Ⅲ-7, Müllen G1 dendron (CD_2Cl_2)



Müllen G2-OH (CD_2Cl_2)



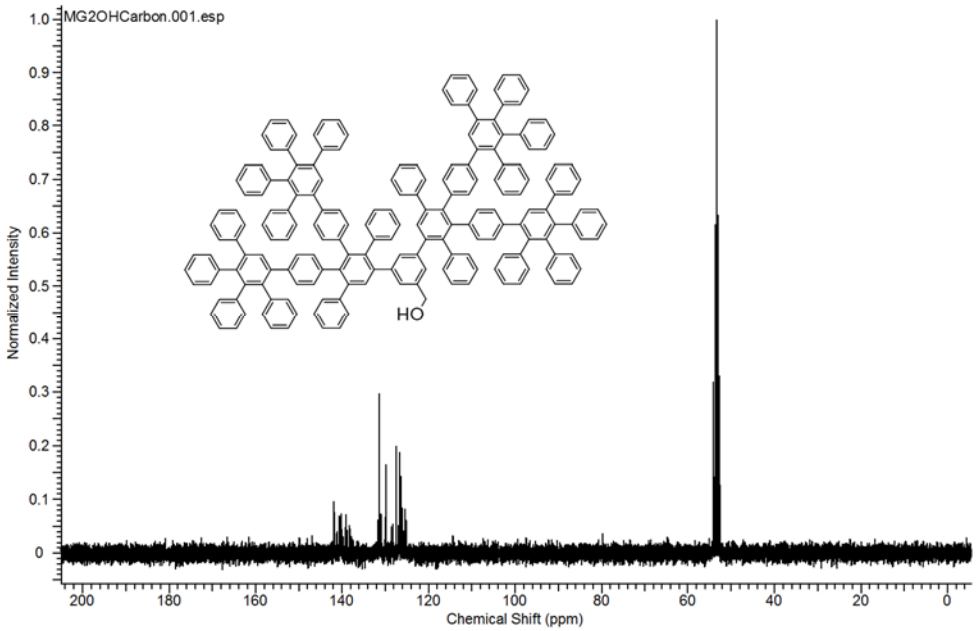
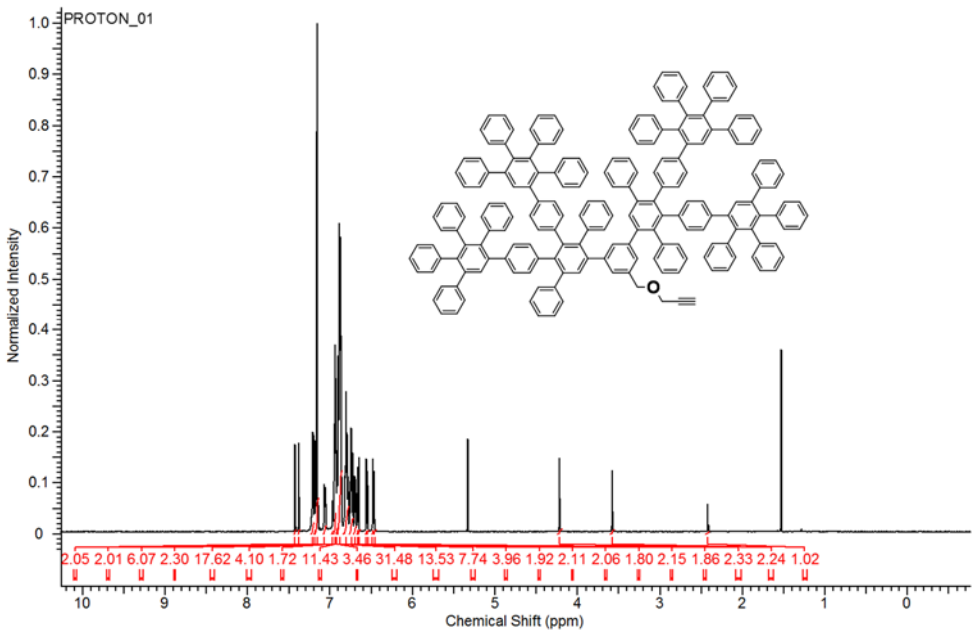


Figure Ⅲ-7, Müllen G2 dendron (CD_2Cl_2)



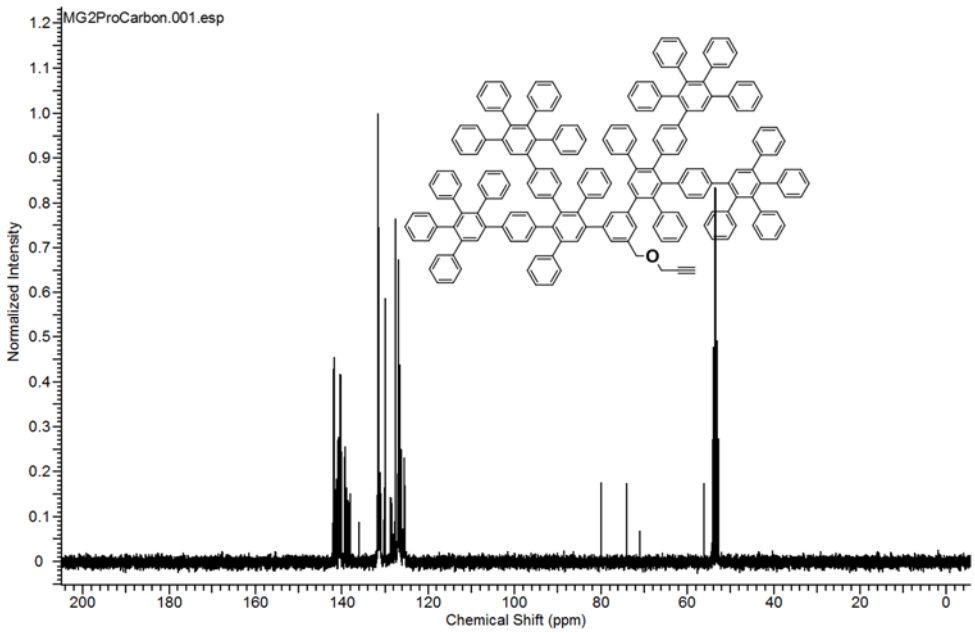


Figure Ⅲ-7, Thiophene G2 dendron ($CDCl_3$)

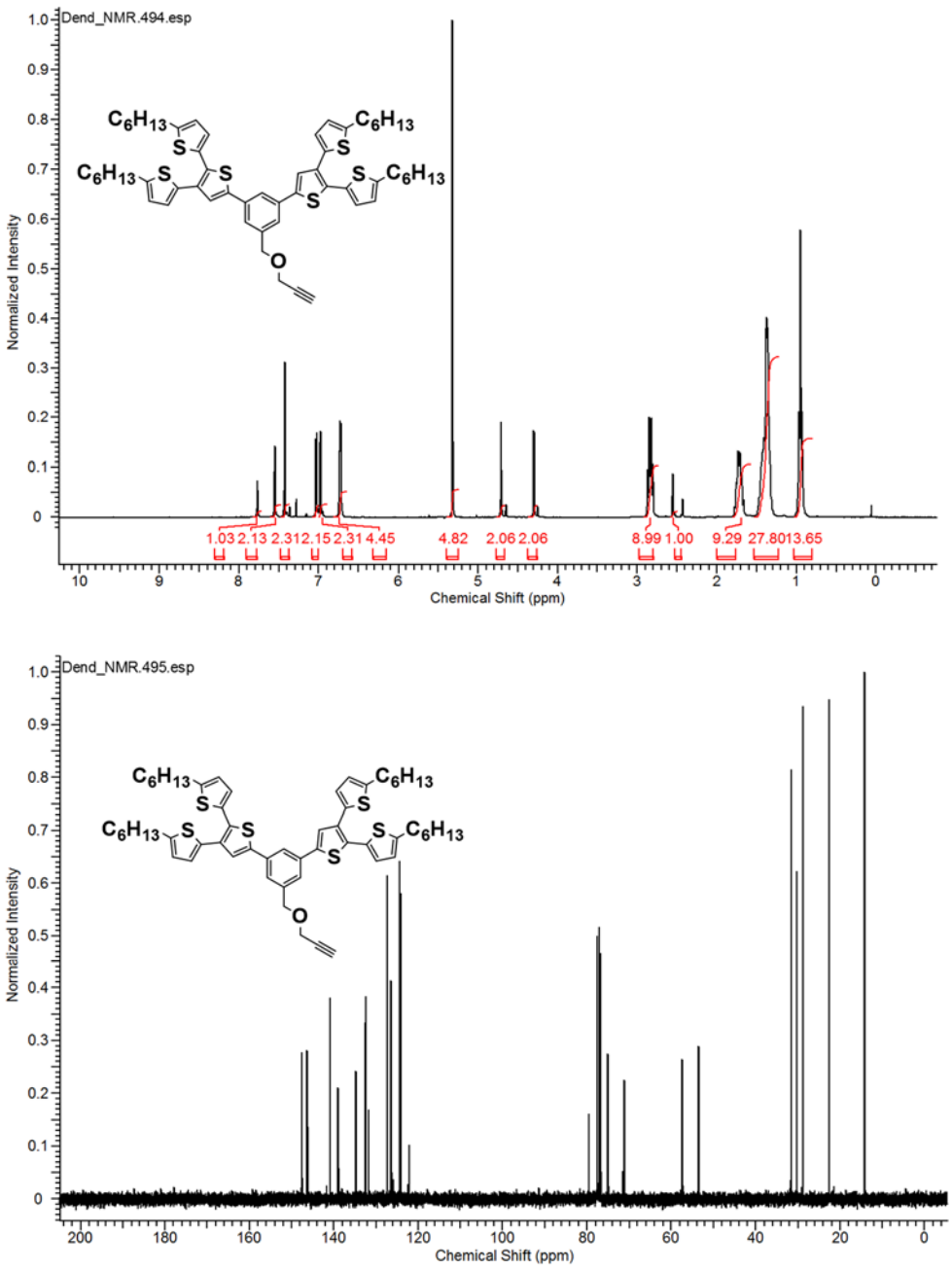
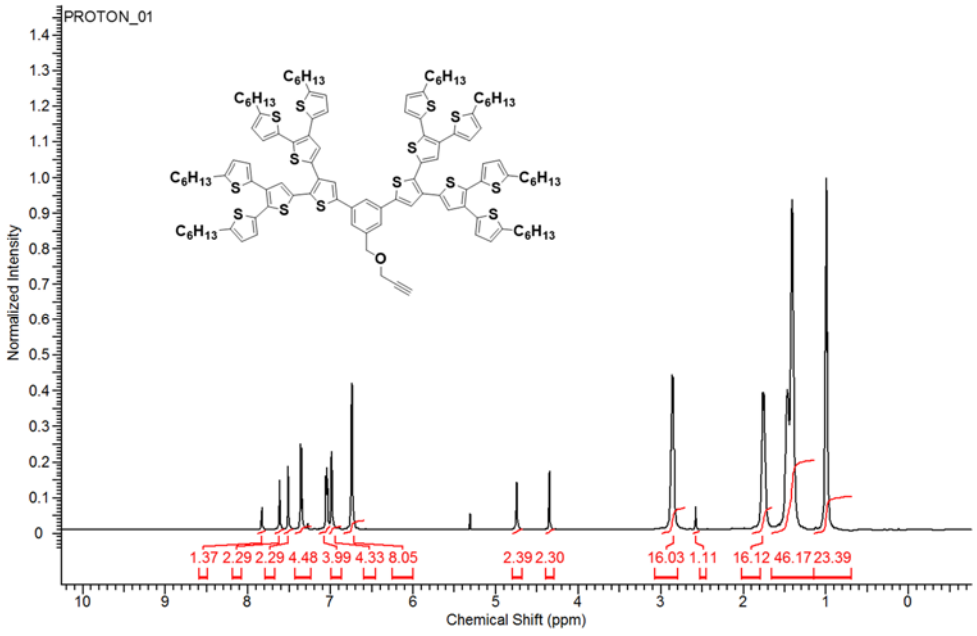
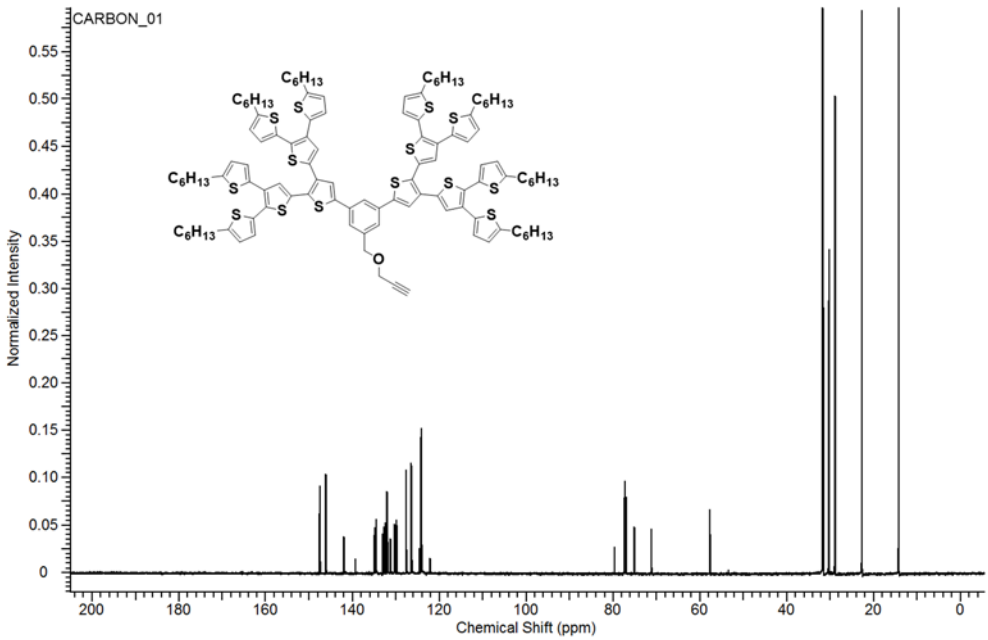


Figure Ⅲ-7, Thiophene G3 dendron ($CDCl_3$)





^{1}H NMR and ^{13}C NMR Spectra of graft polymers

Table Ⅲ-2, entry 1 ($CDCl_3$)

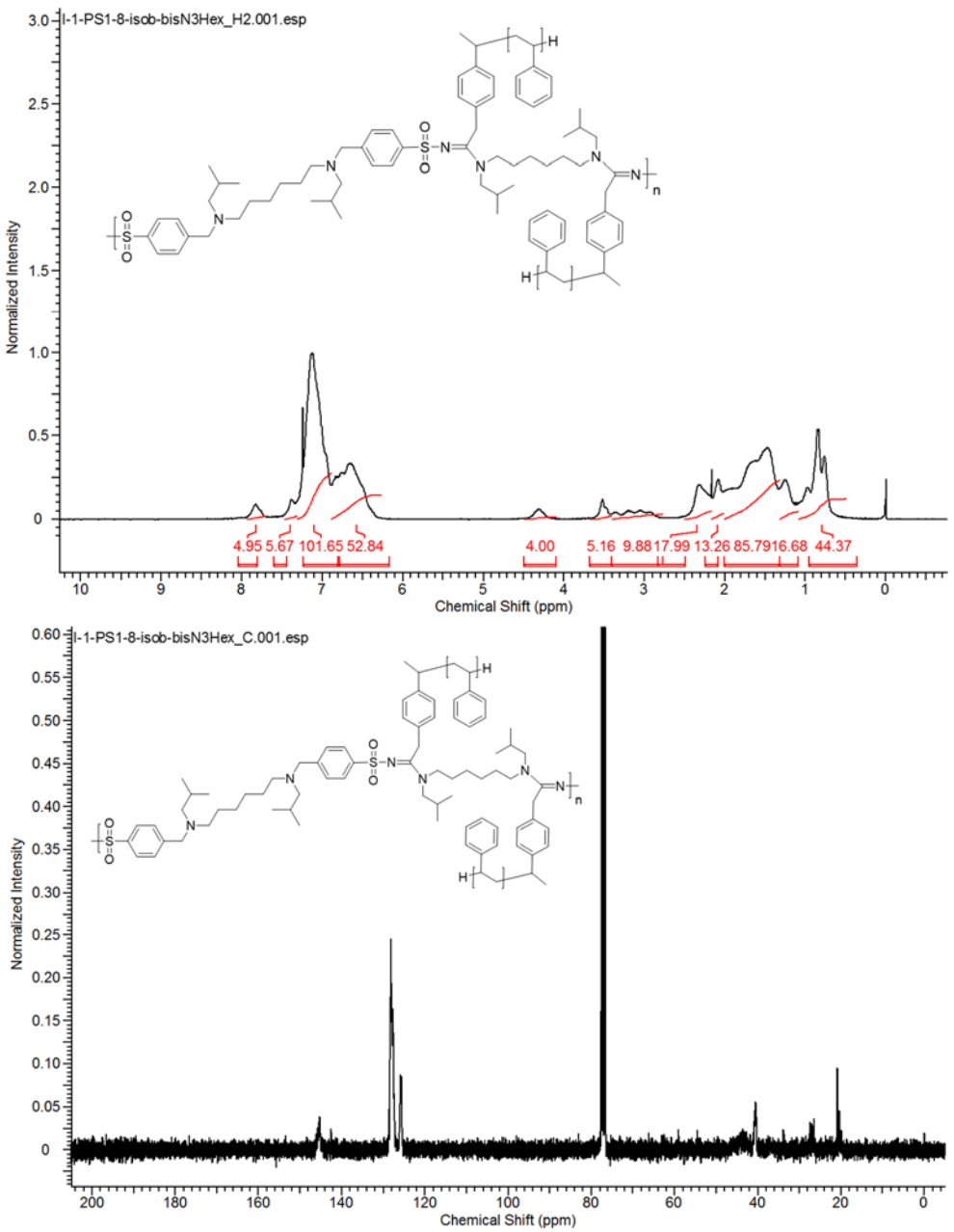
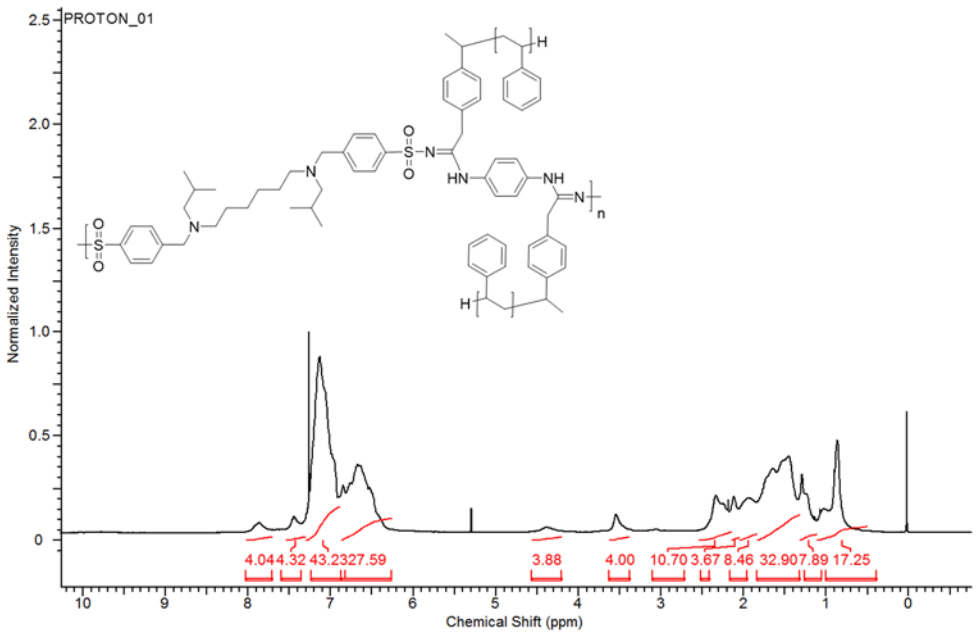


Table Ⅲ-2, entry 2 ($CDCl_3$)



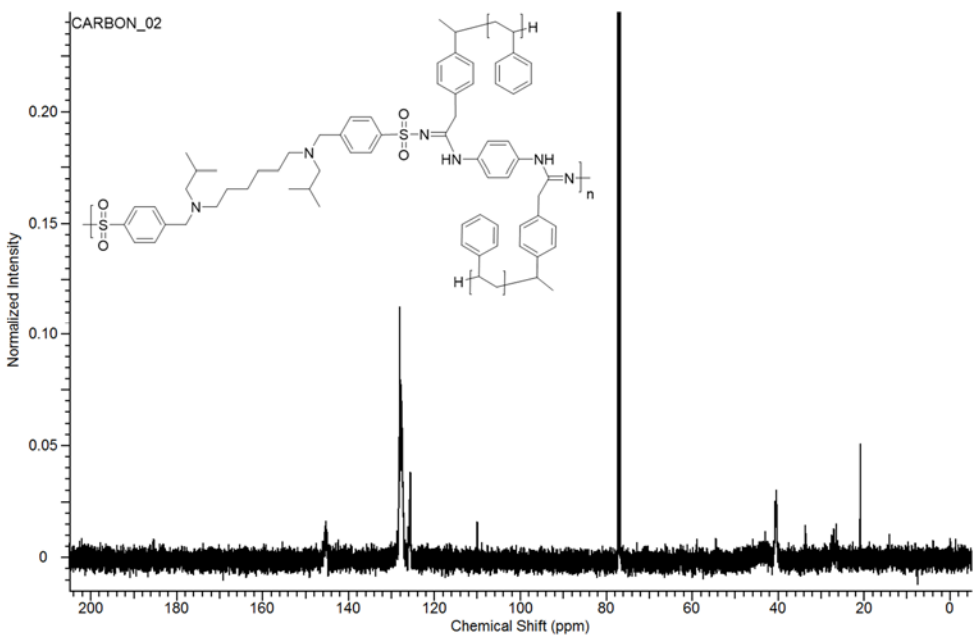
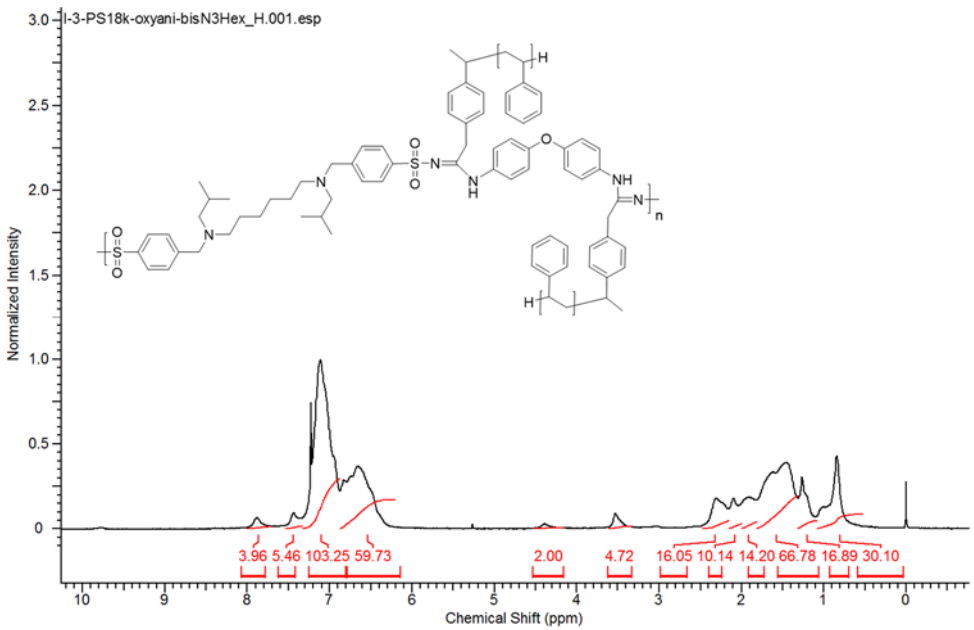


Table Ⅲ-2, entry 3 ($CDCl_3$)



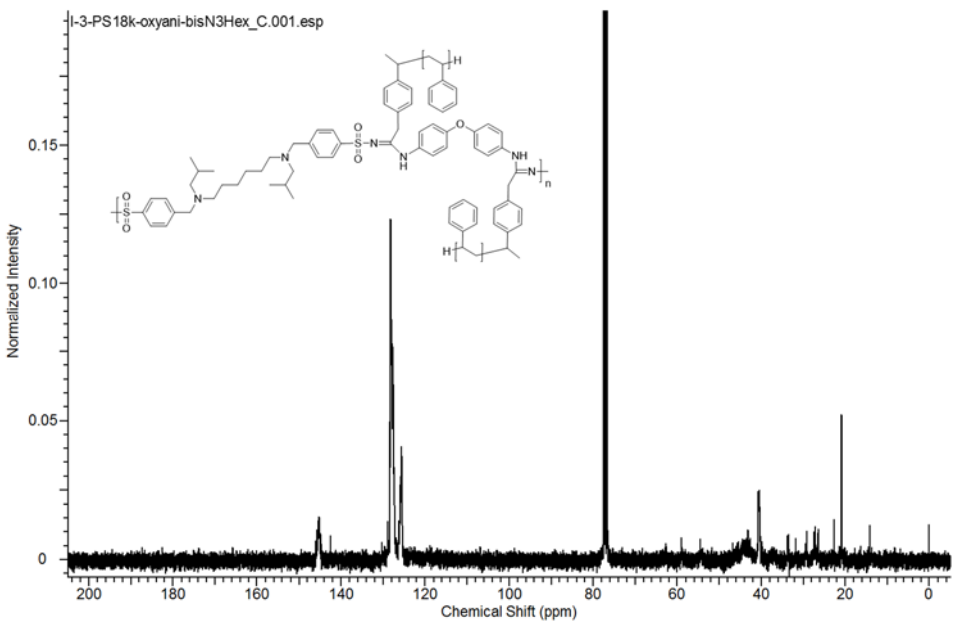
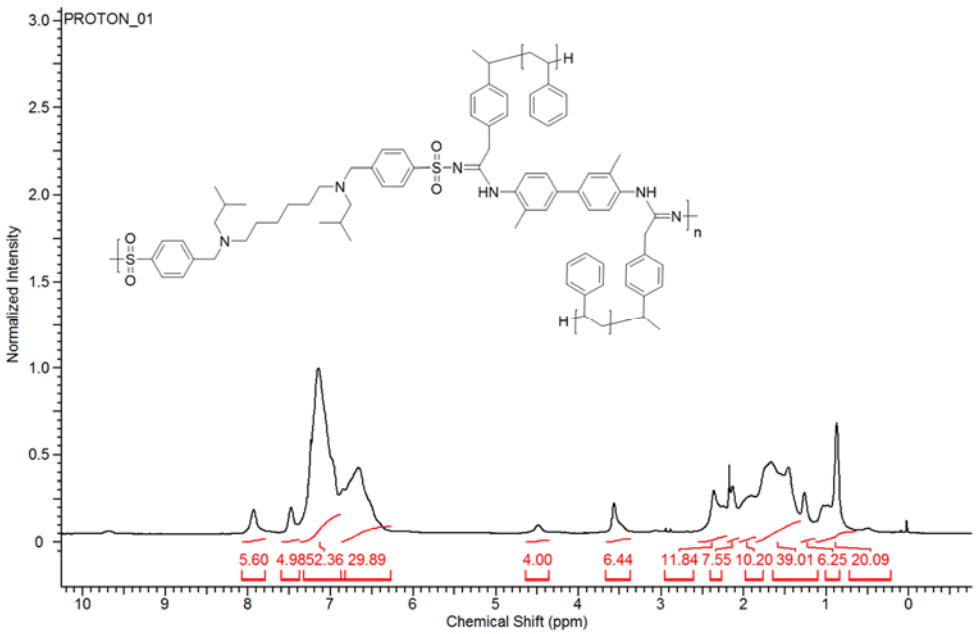


Table Ⅲ-2, entry 4 ($CDCl_3$)



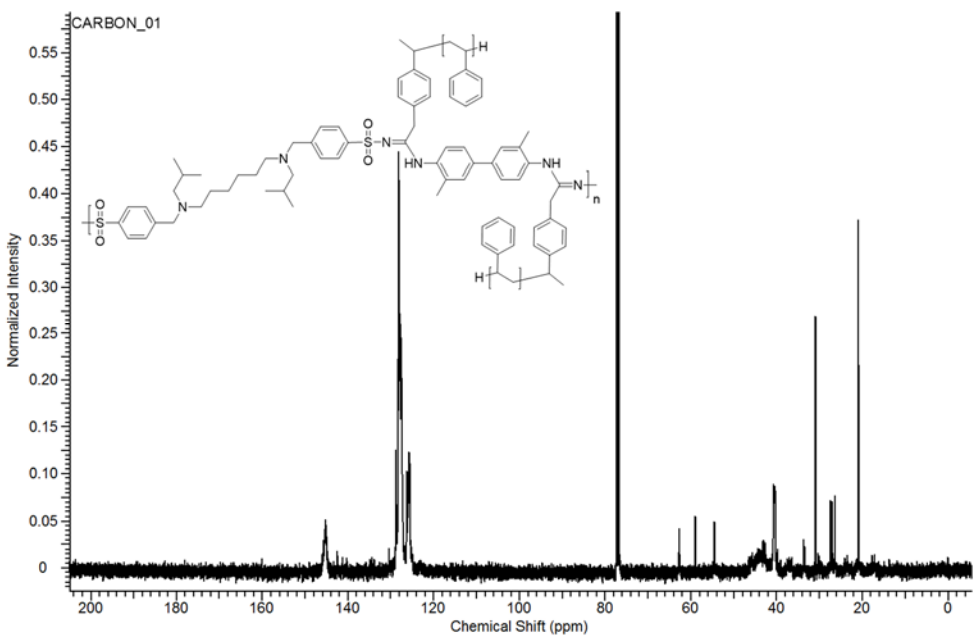
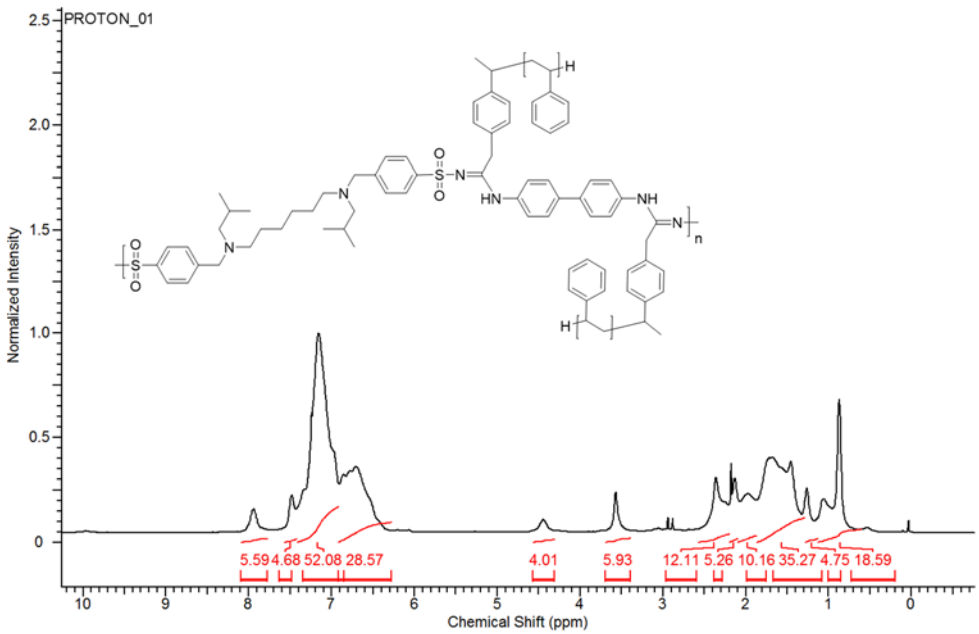


Table Ⅲ-2, entry 5 ($CDCl_3$)



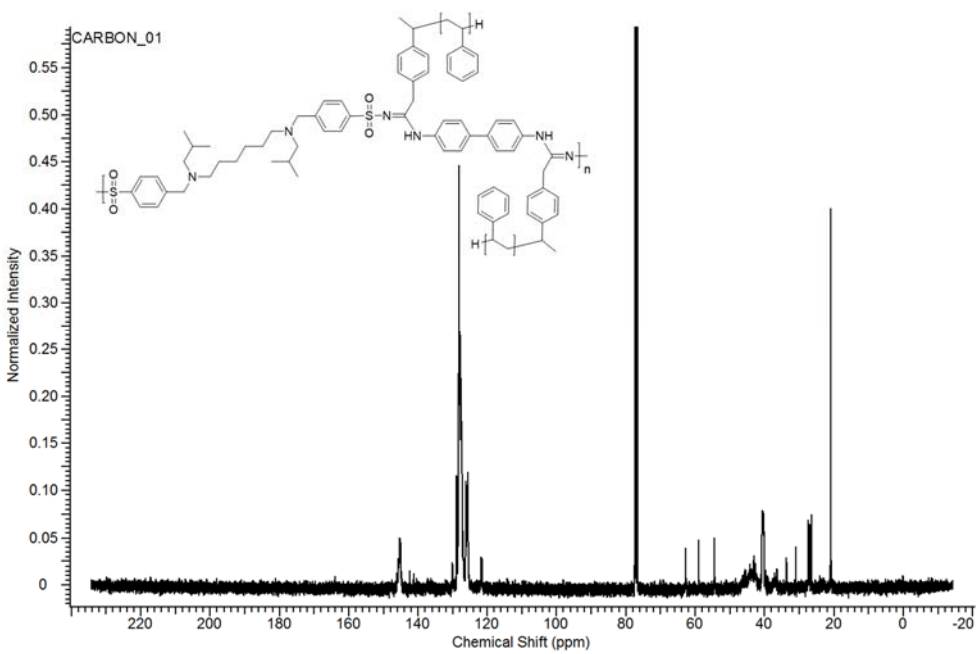
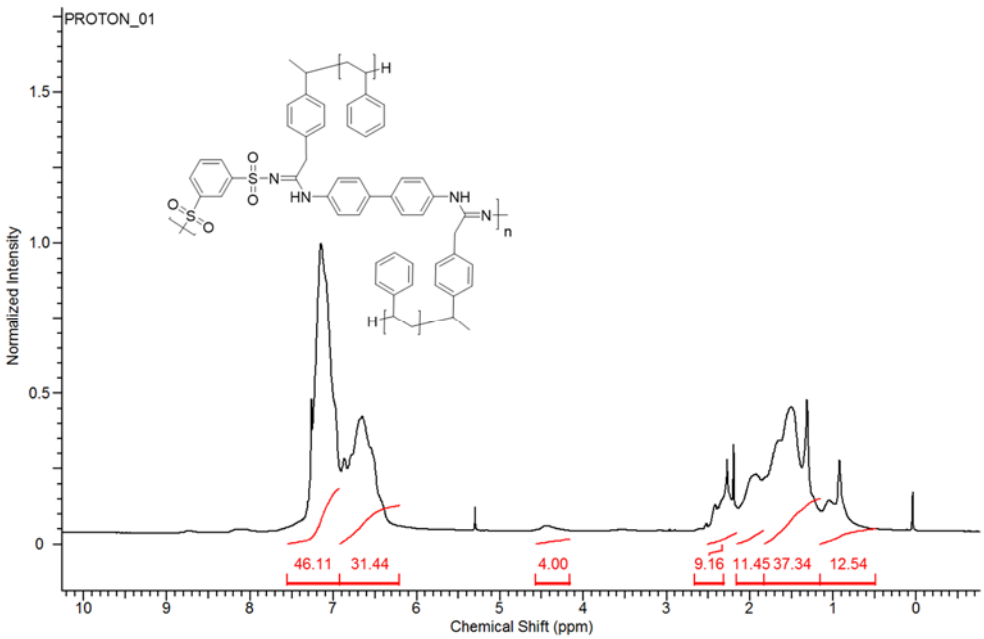
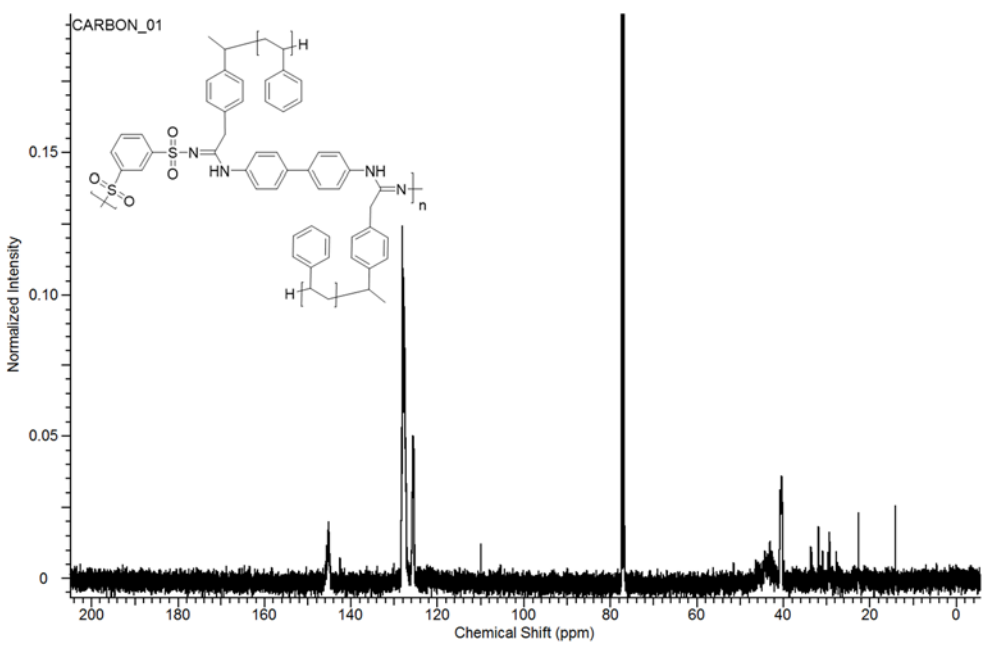


Table Ⅲ-2, entry 6 ($CDCl_3$)





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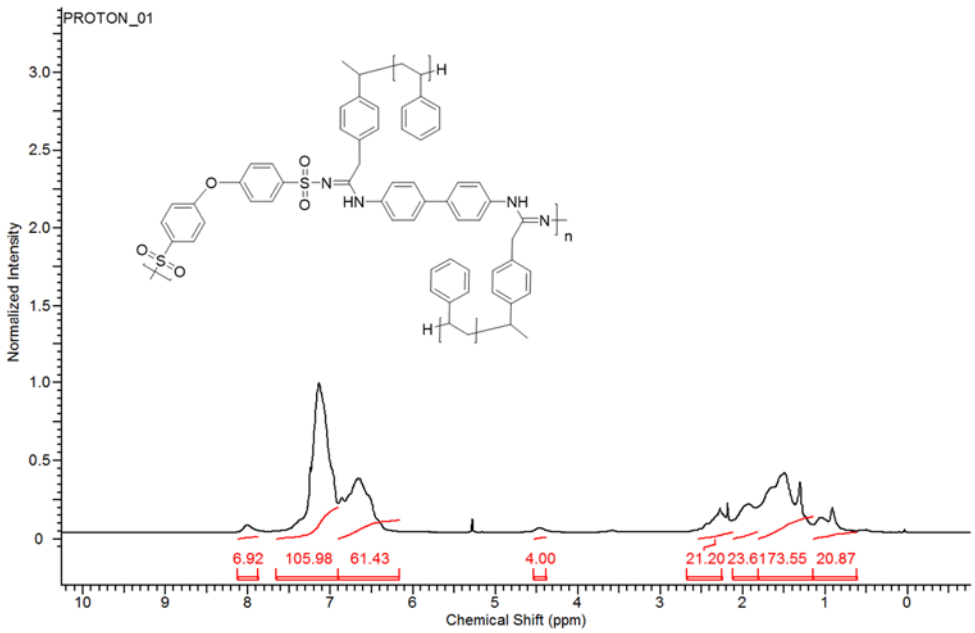


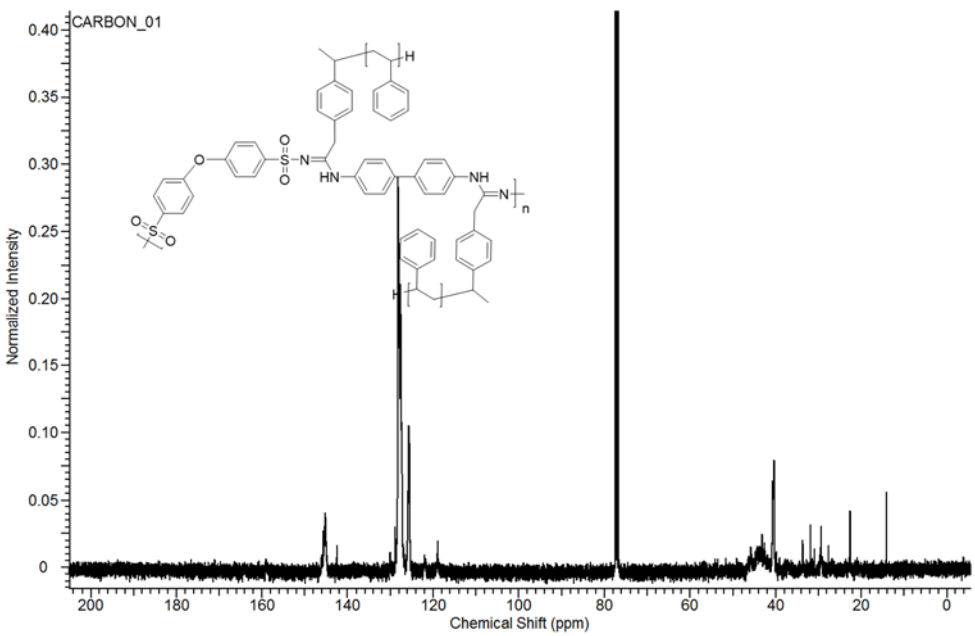
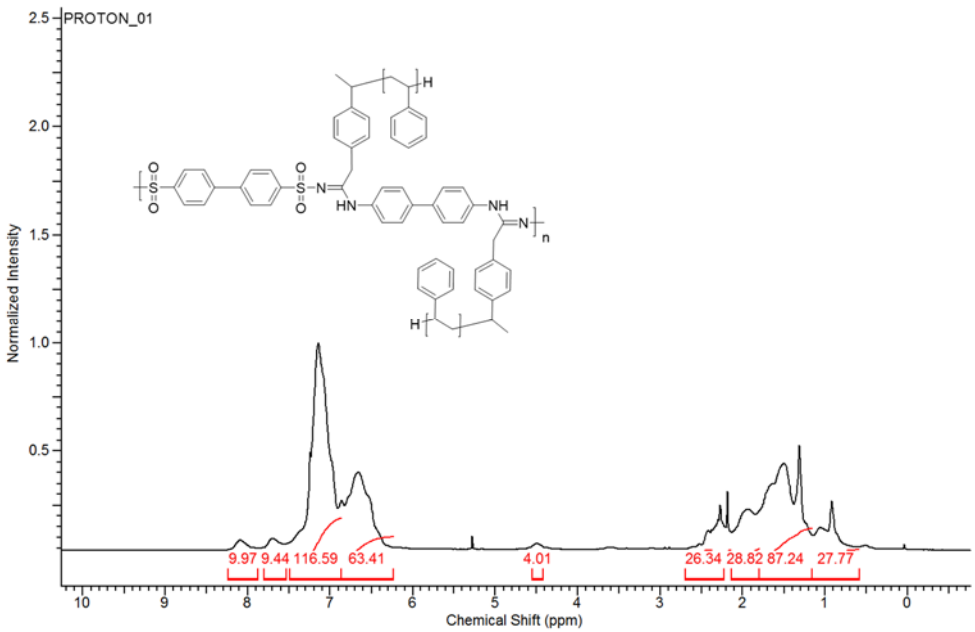
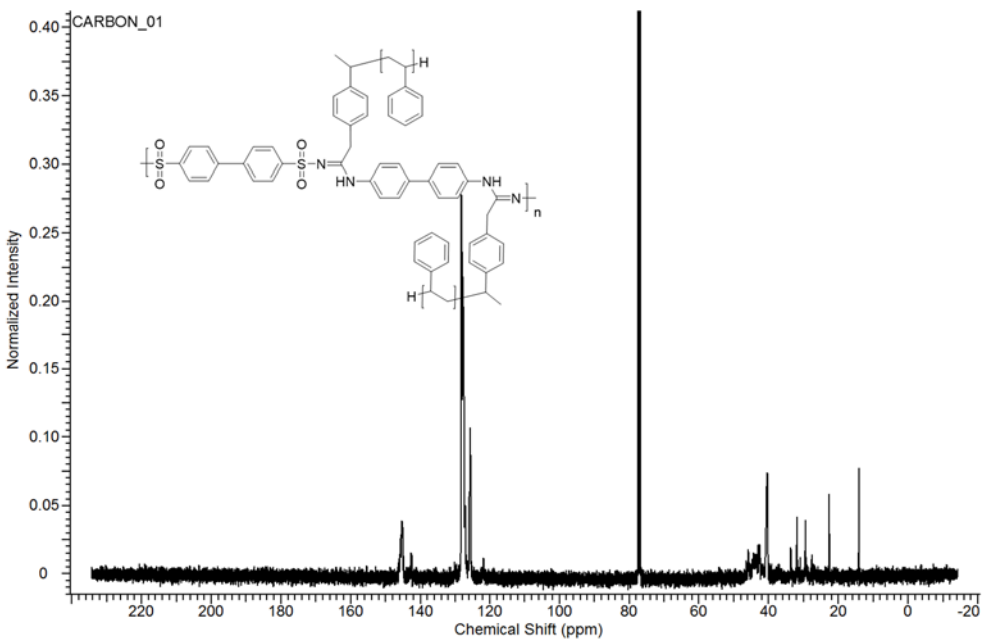


Table Ⅲ-2, entry 8 ($CDCl_3$)





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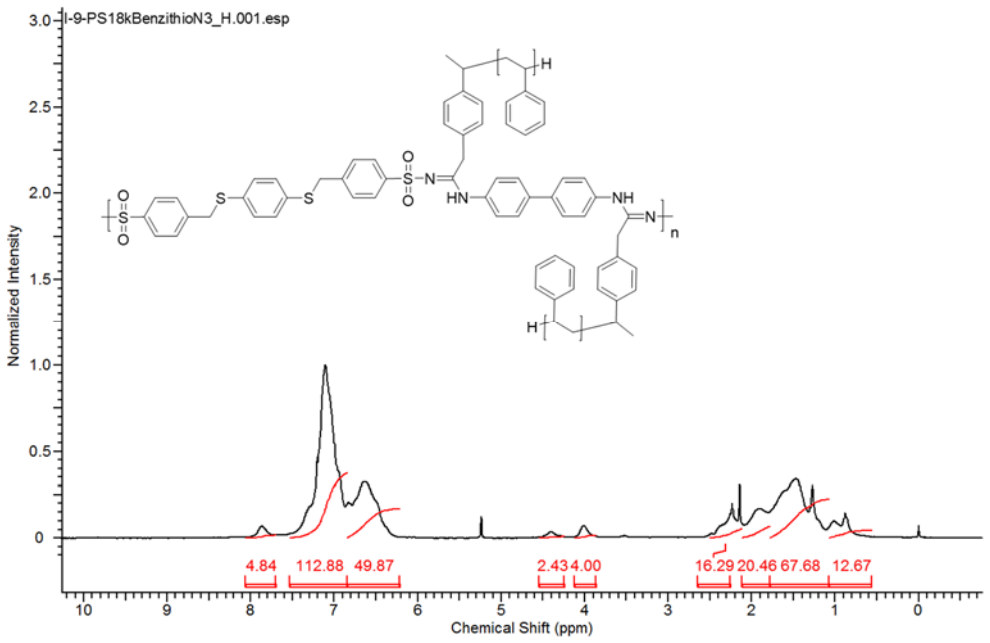

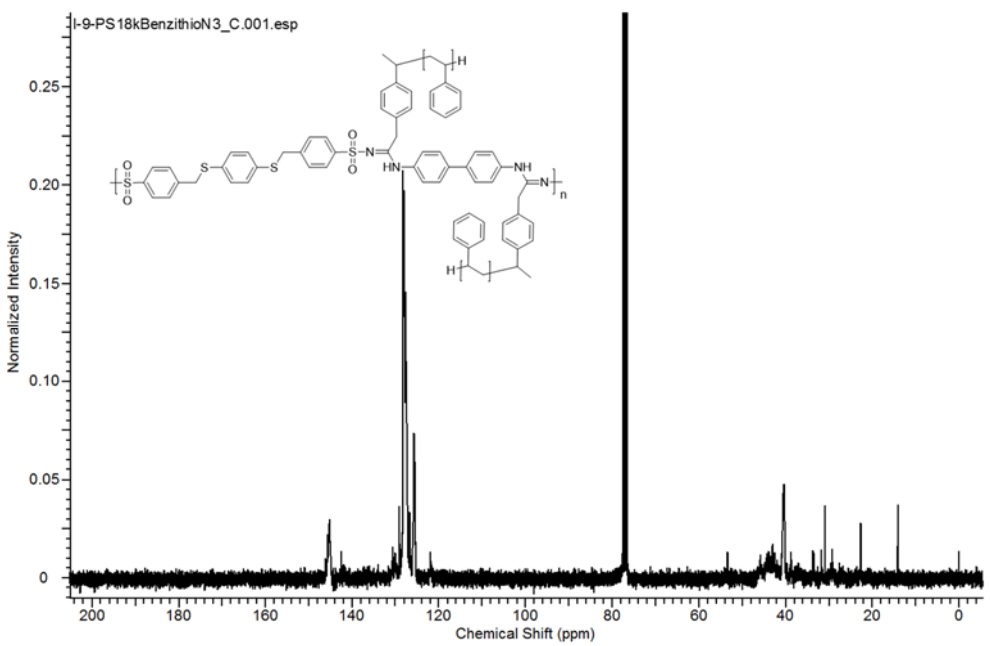

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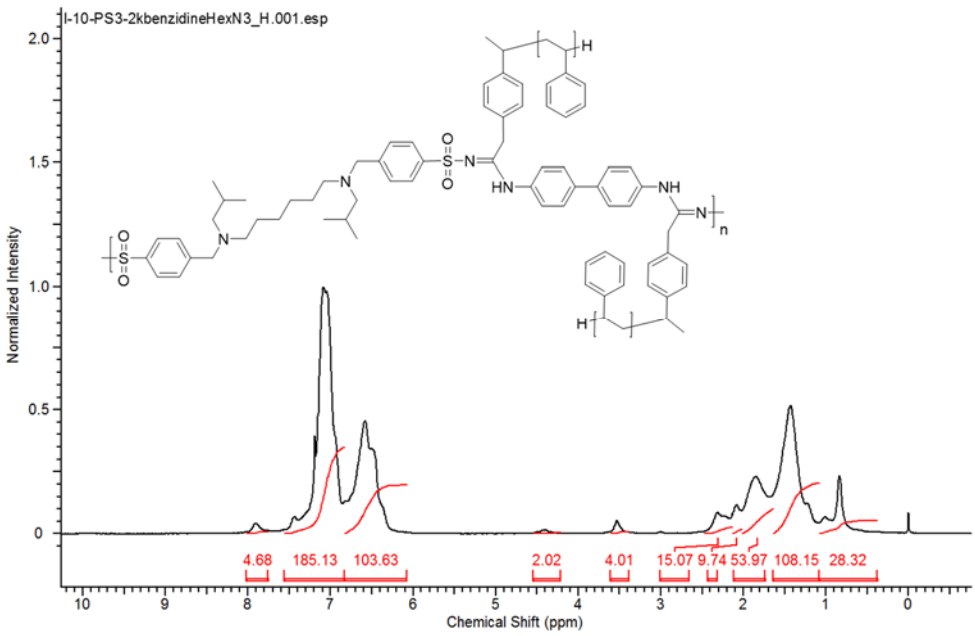


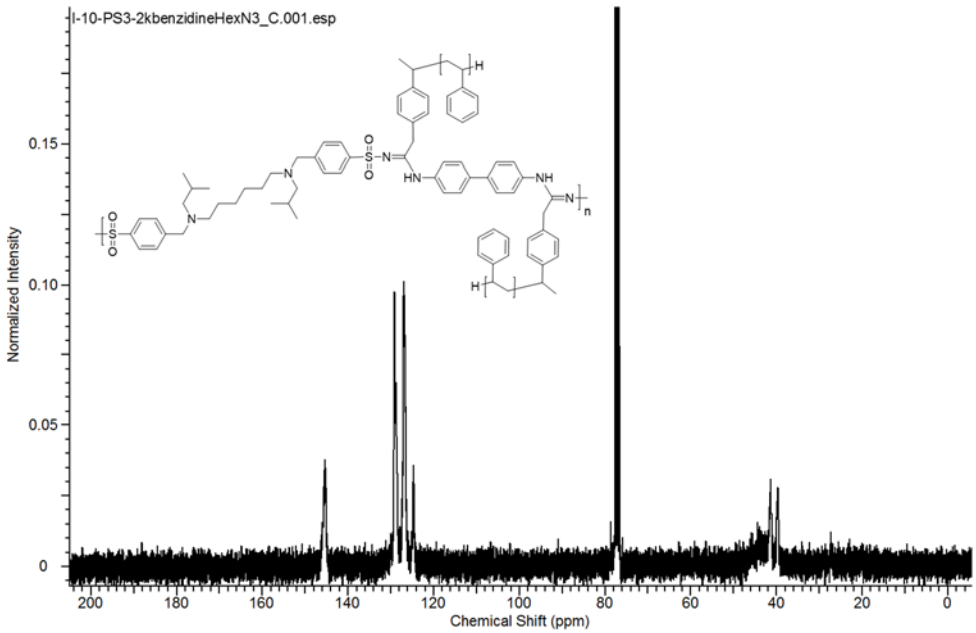
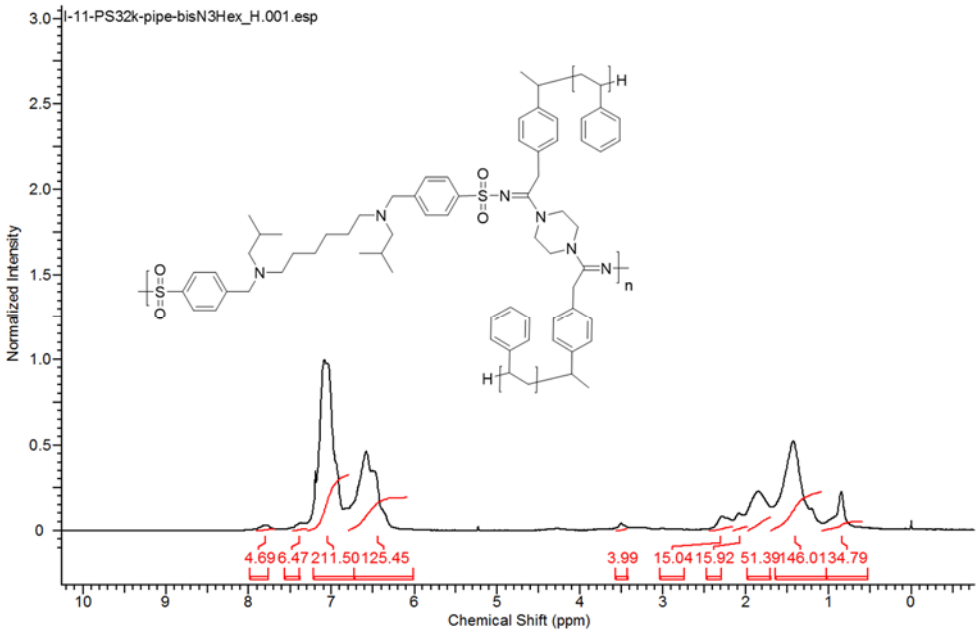


Table Ⅲ-2, entry 11 ($CDCl_3$)



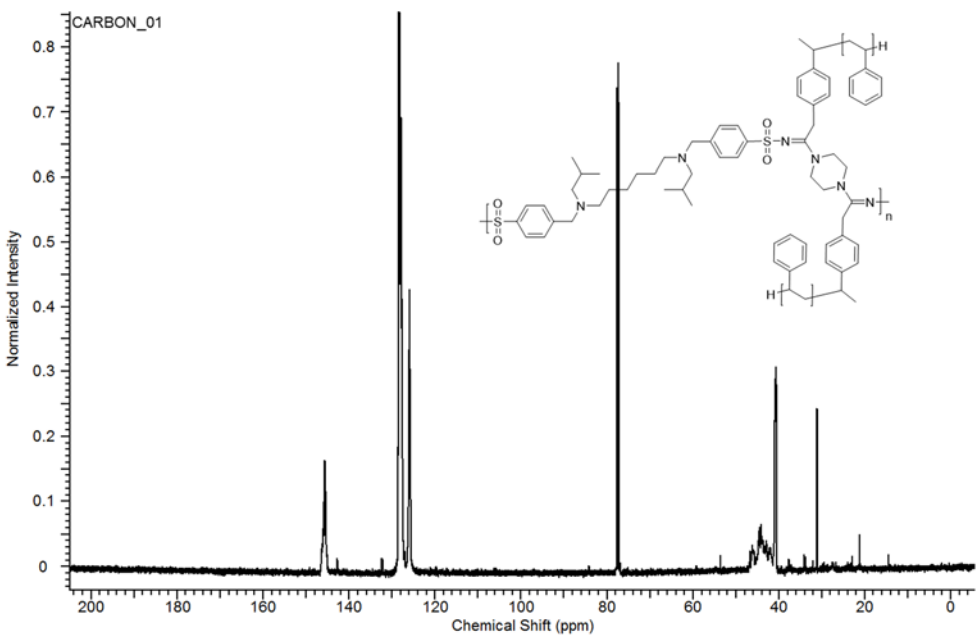
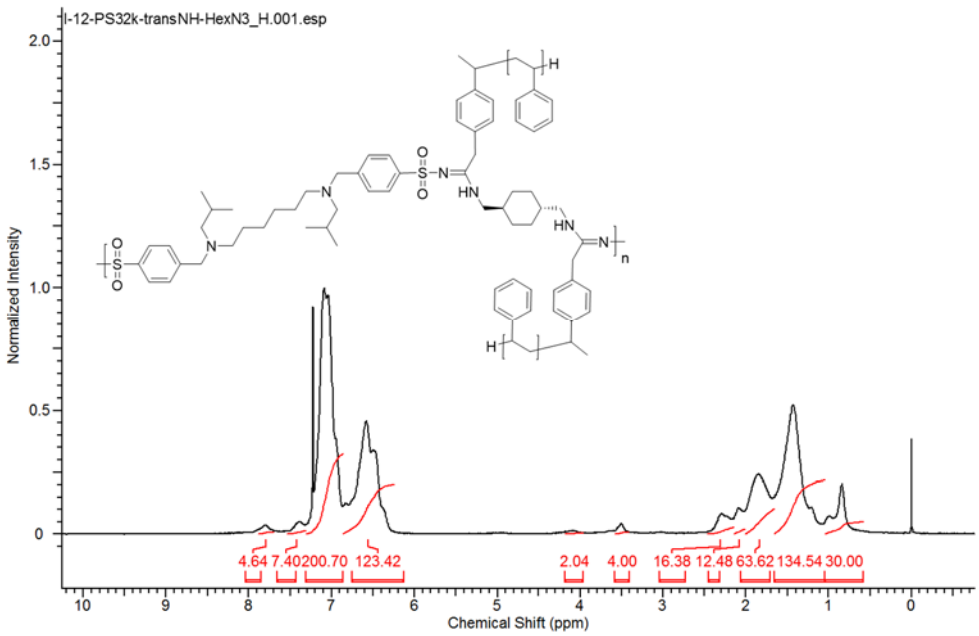


Table Ⅲ-2, entry 12 ($CDCl_3$)



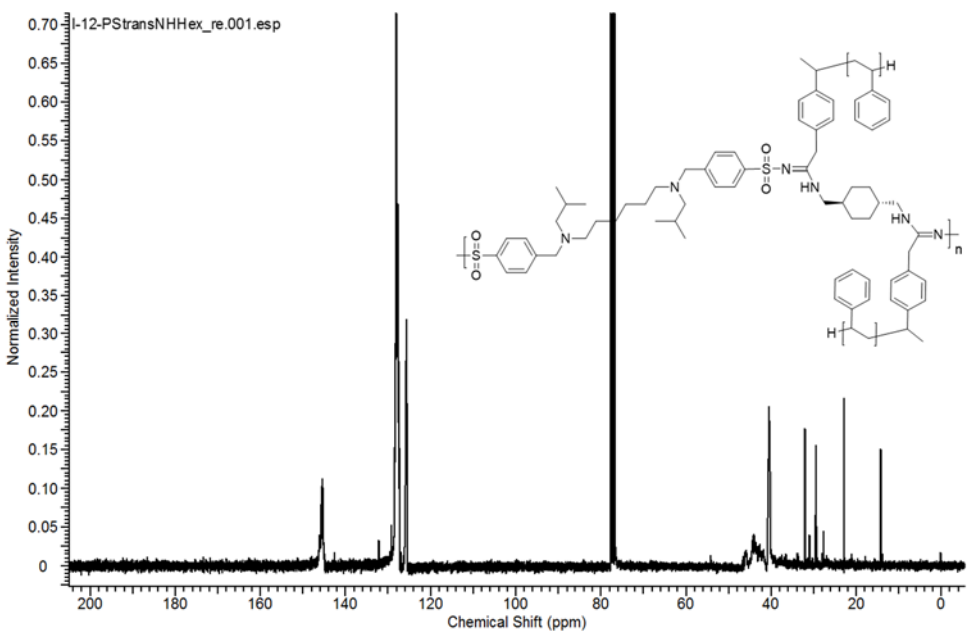
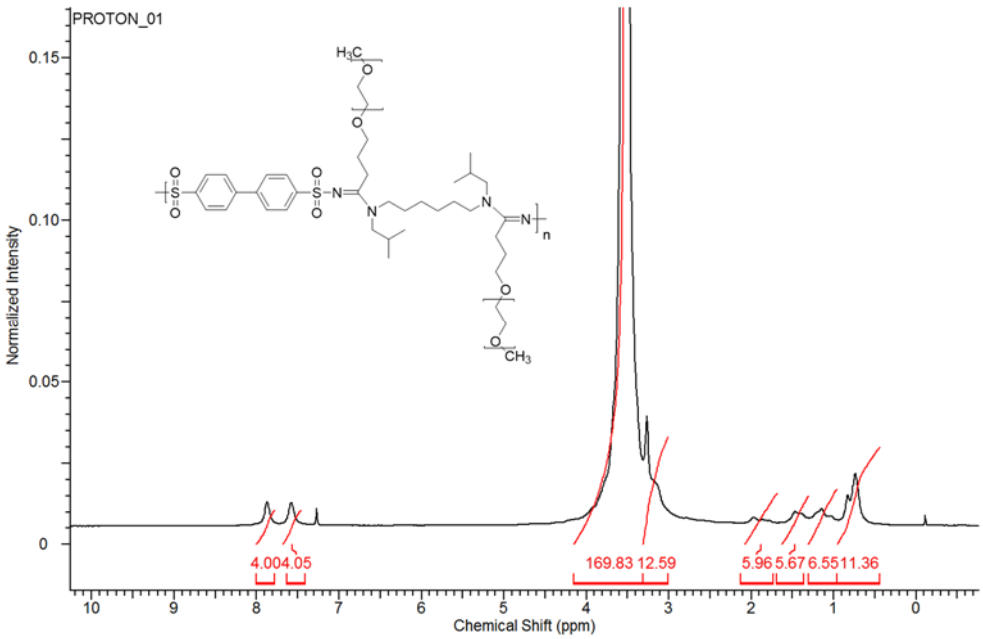


Table Ⅲ-2, entry 13 ($CDCl_3$)



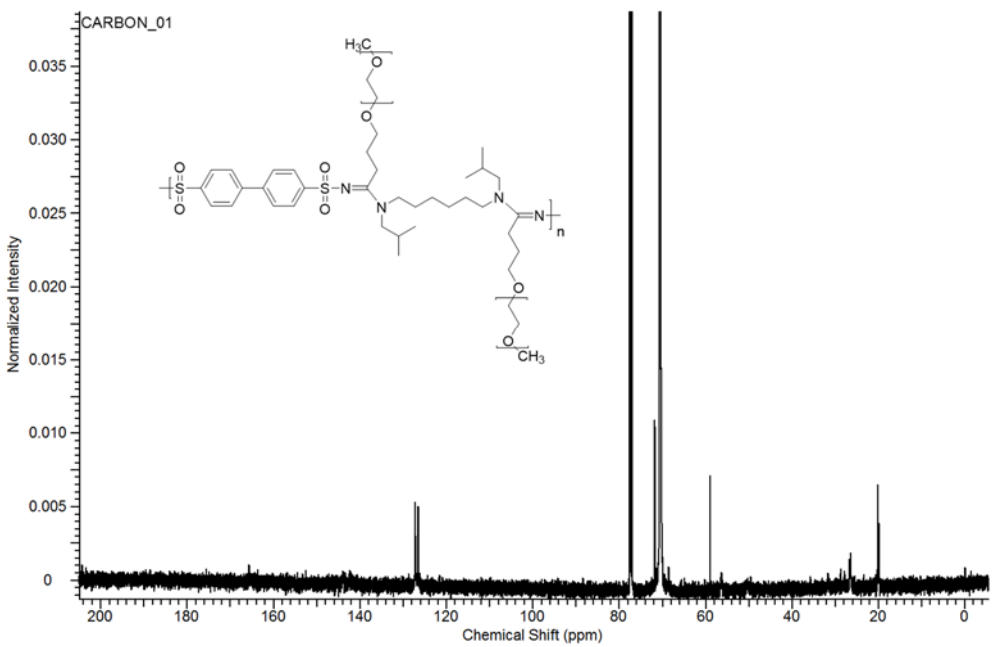
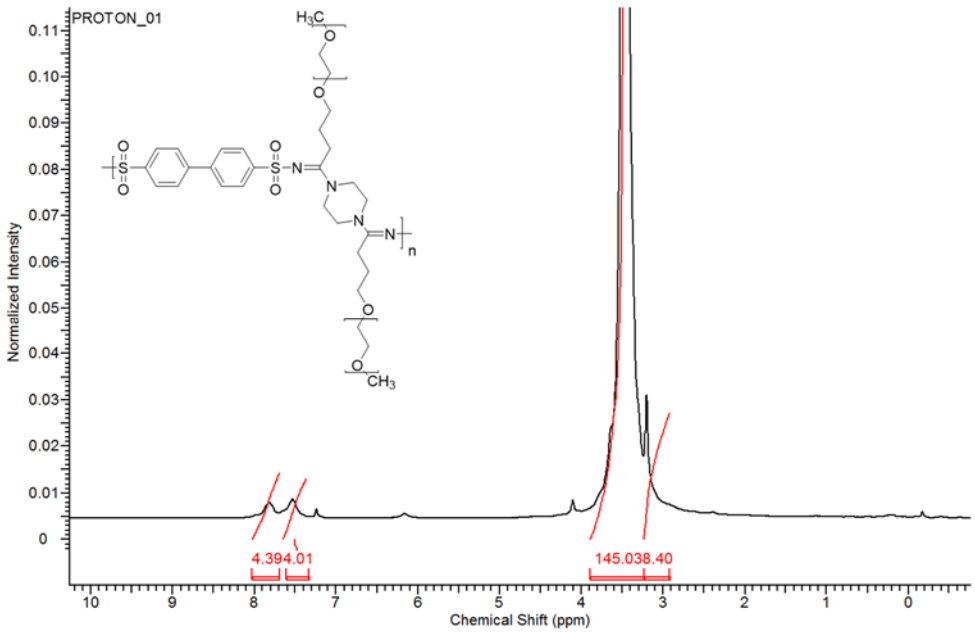


Table Ⅲ-2, entry 14 ($CDCl_3$)



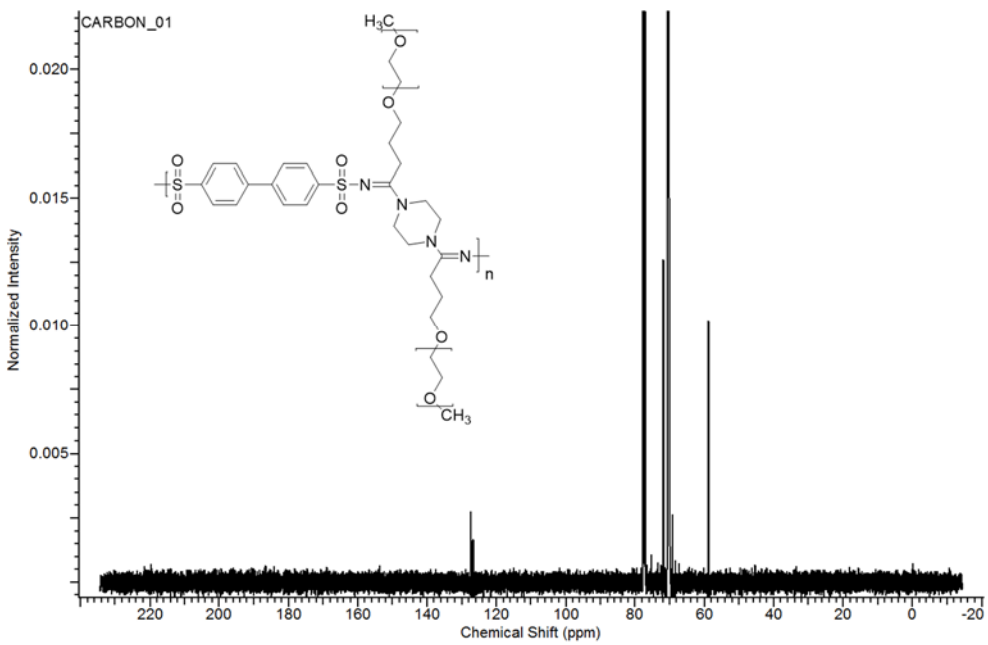
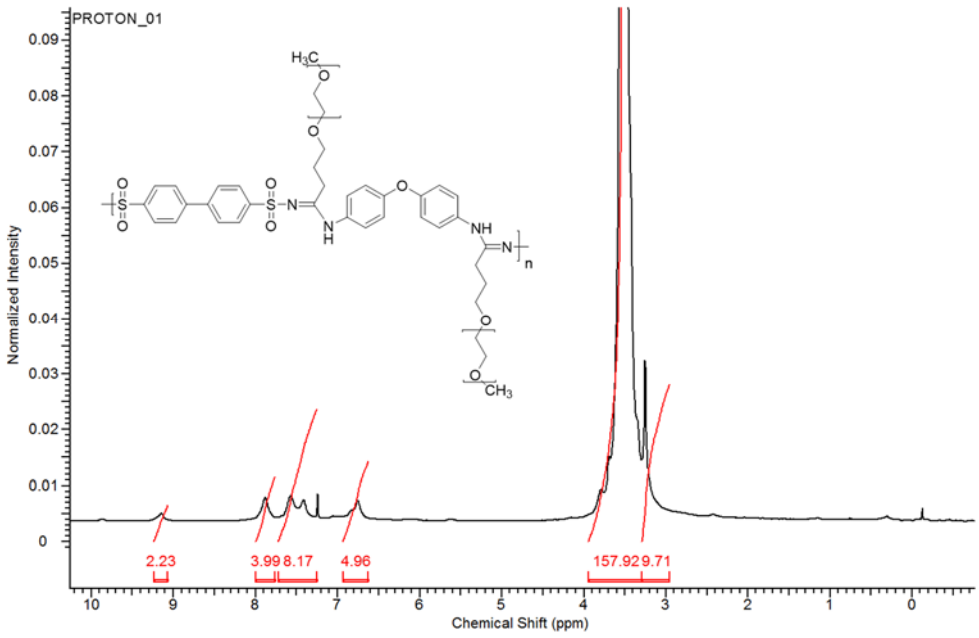


Table Ⅲ-2, entry 15 ($CDCl_3$)



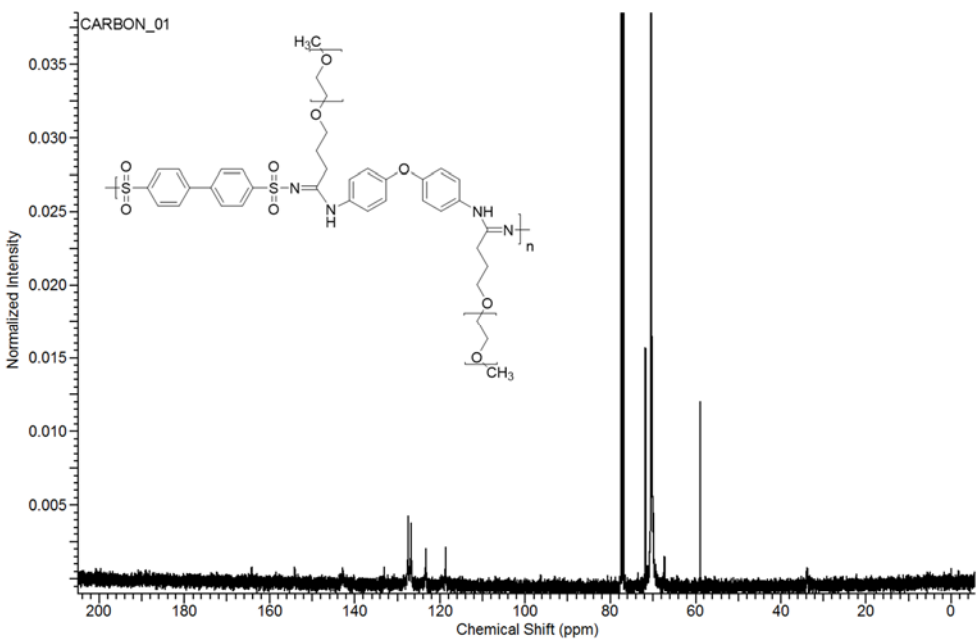
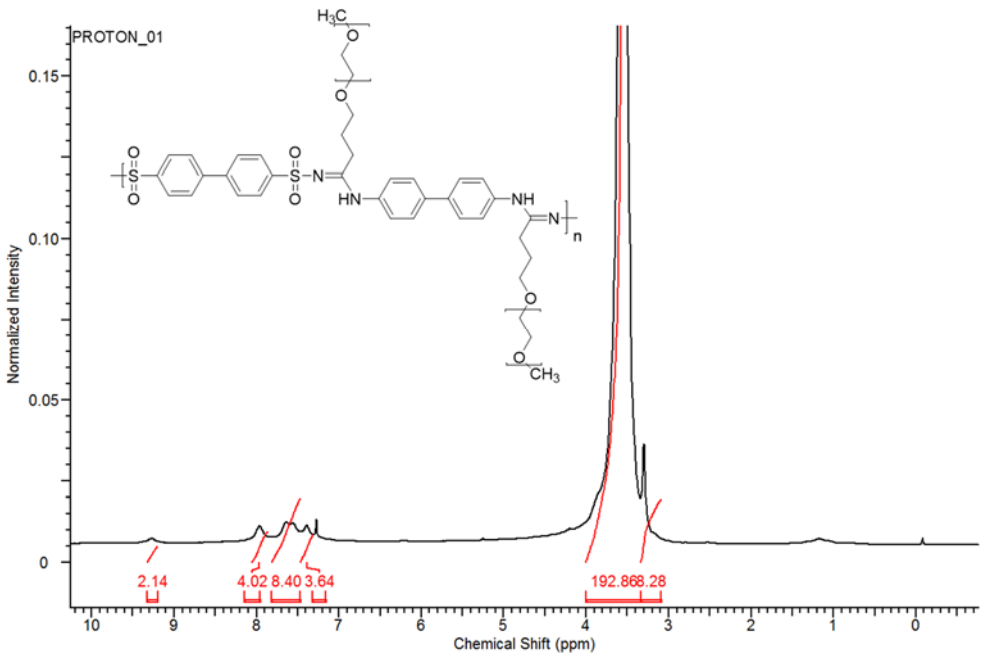


Table Ⅲ-2, entry 16 ($CDCl_3$)



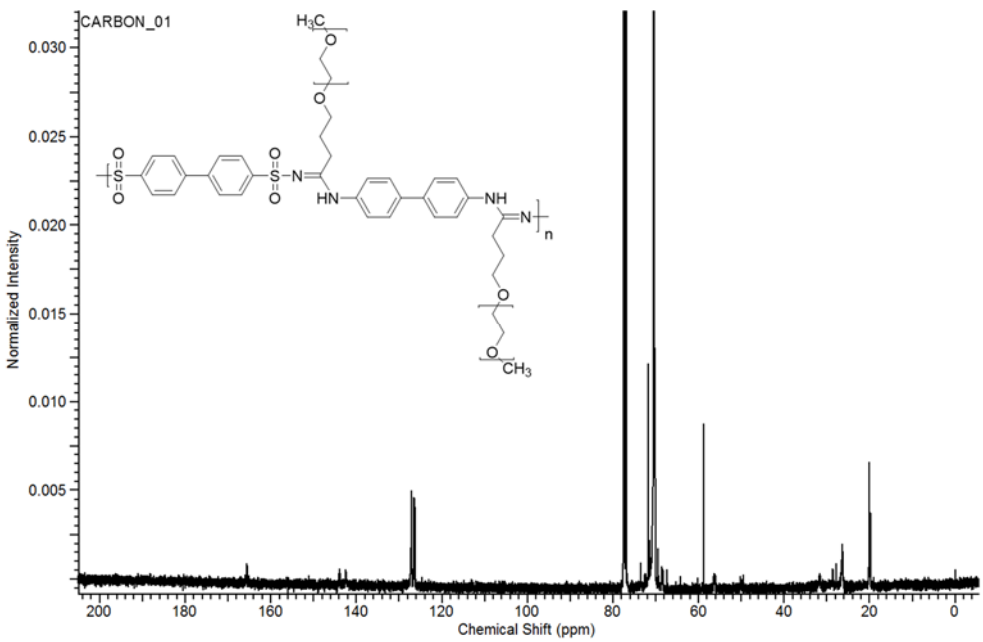
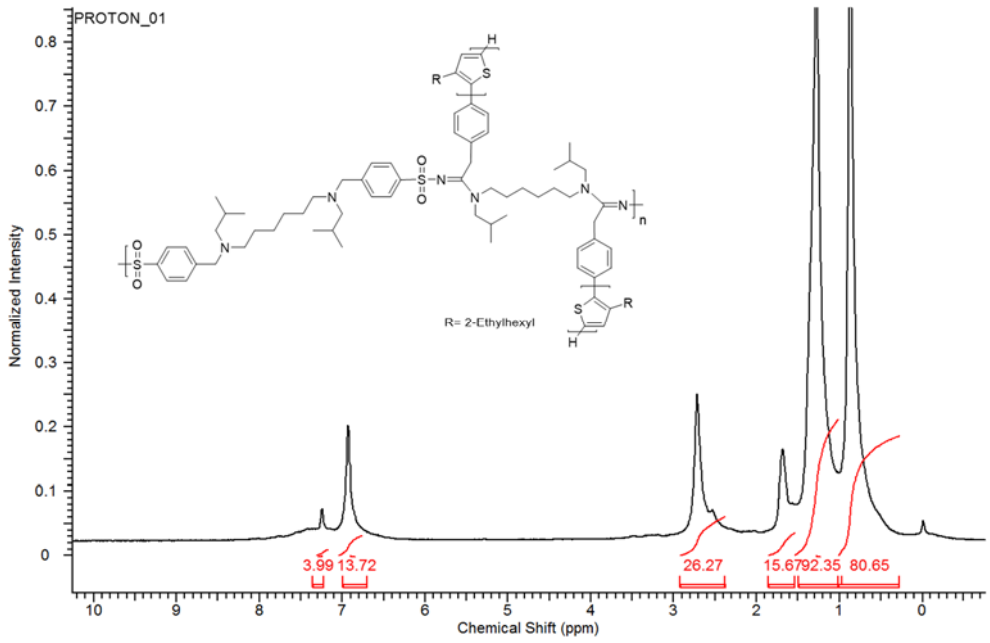


Table Ⅲ-2, entry 17 ($CDCl_3$)



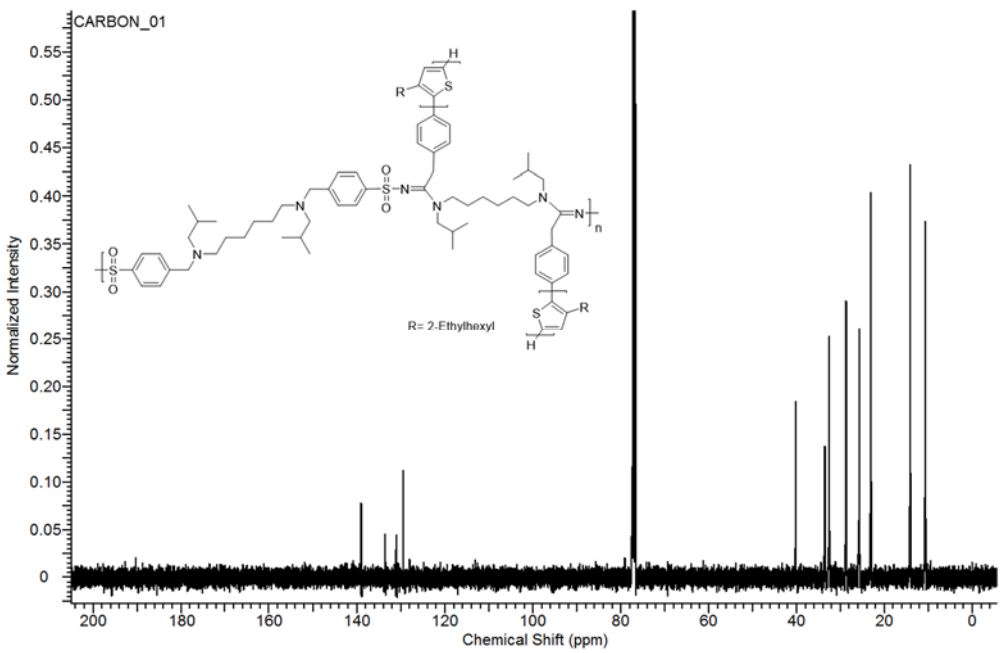
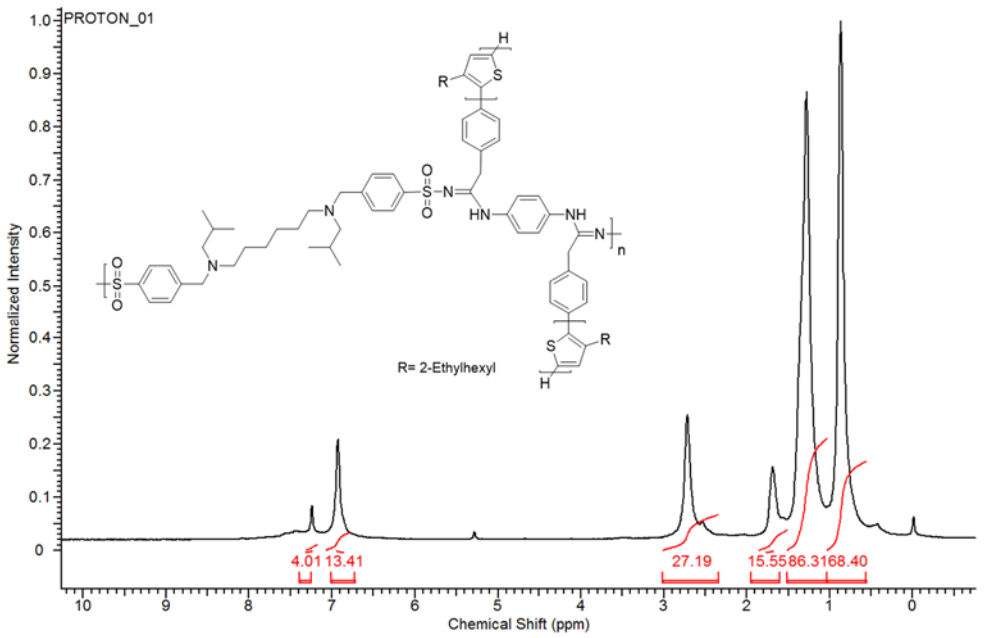
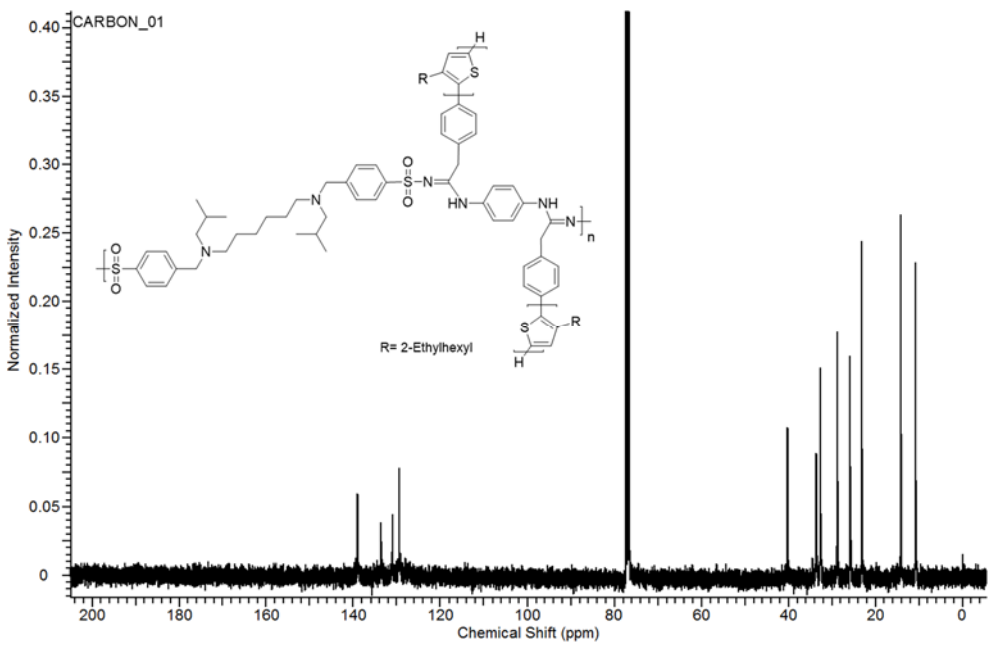


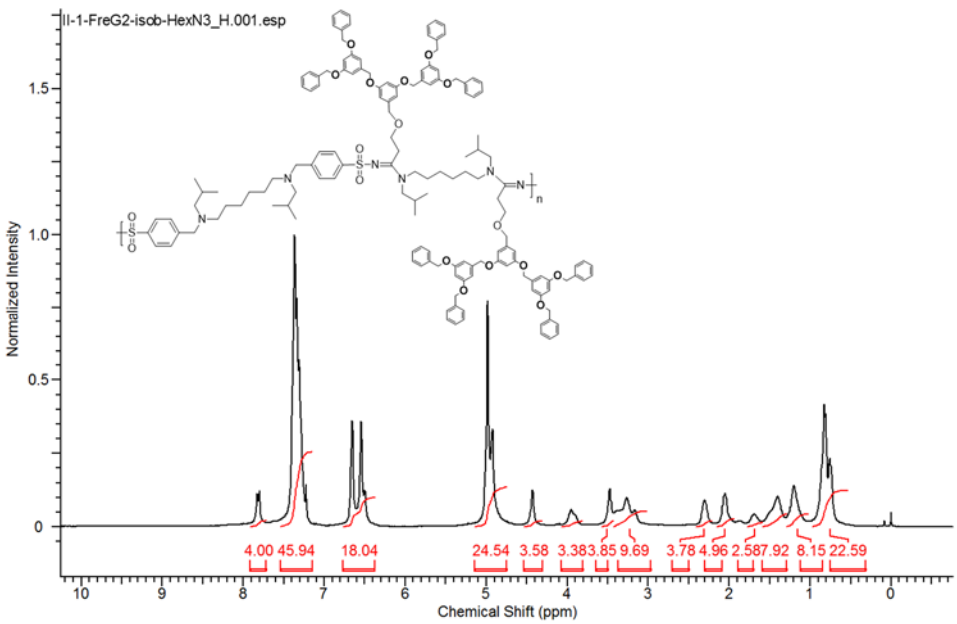
Table Ⅲ-2, entry 18 ($CDCl_3$)





^{1}H NMR and ^{13}C NMR Spectra of dendronized polymers

Table Ⅲ-4, entry 1 ($CDCl_3$)



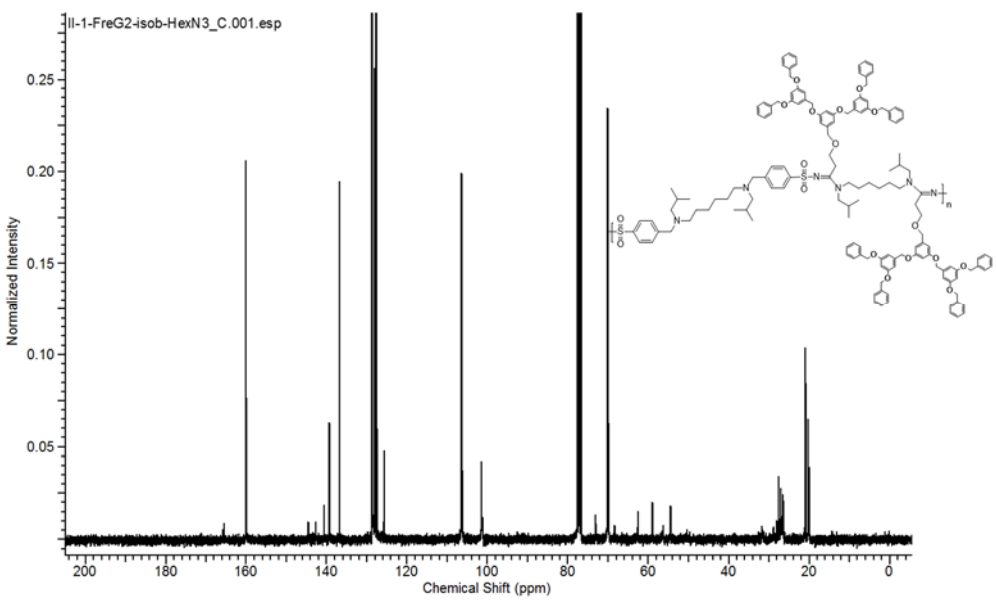


Table Ⅲ-4, entry 2 ($CDCl_3$)

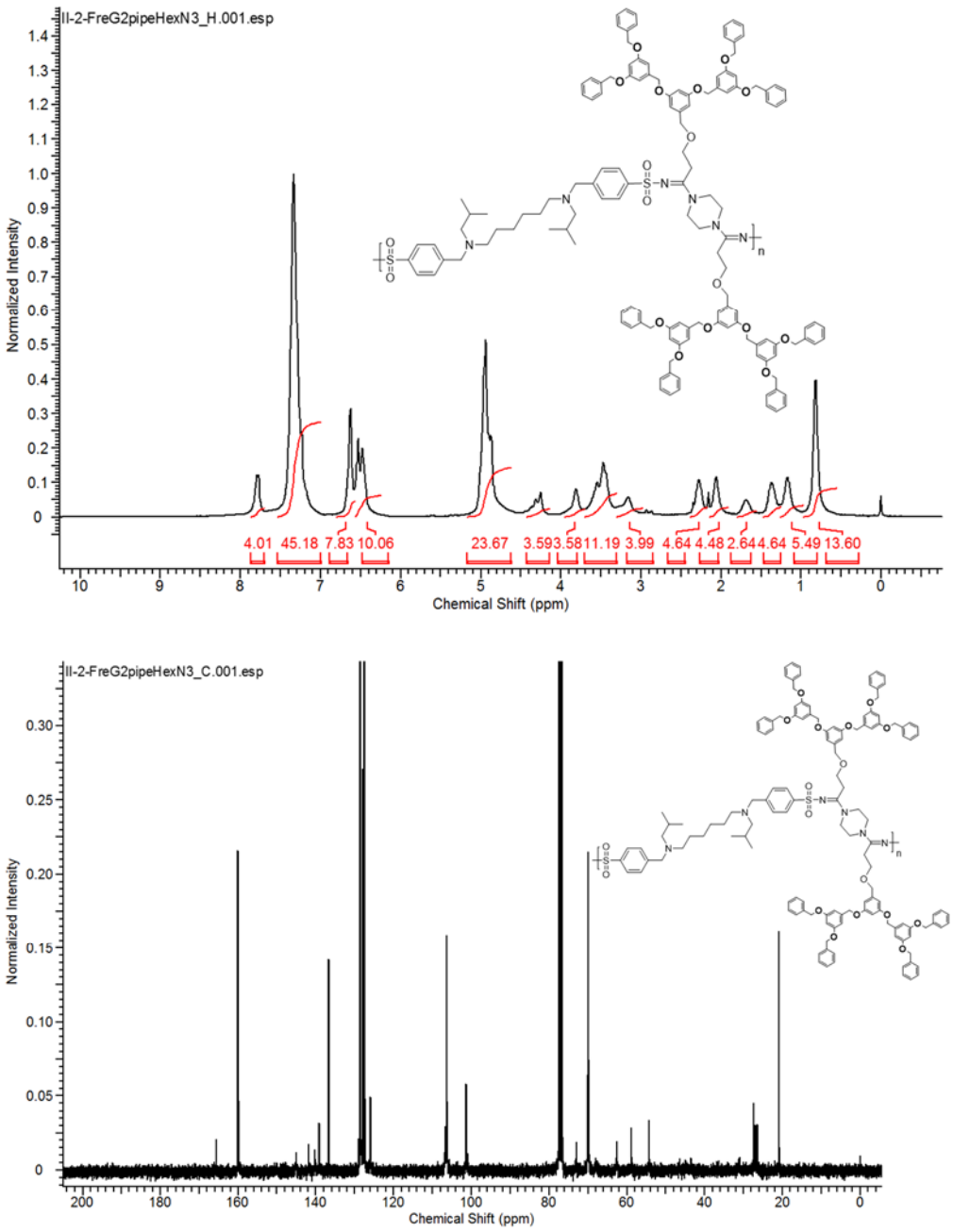
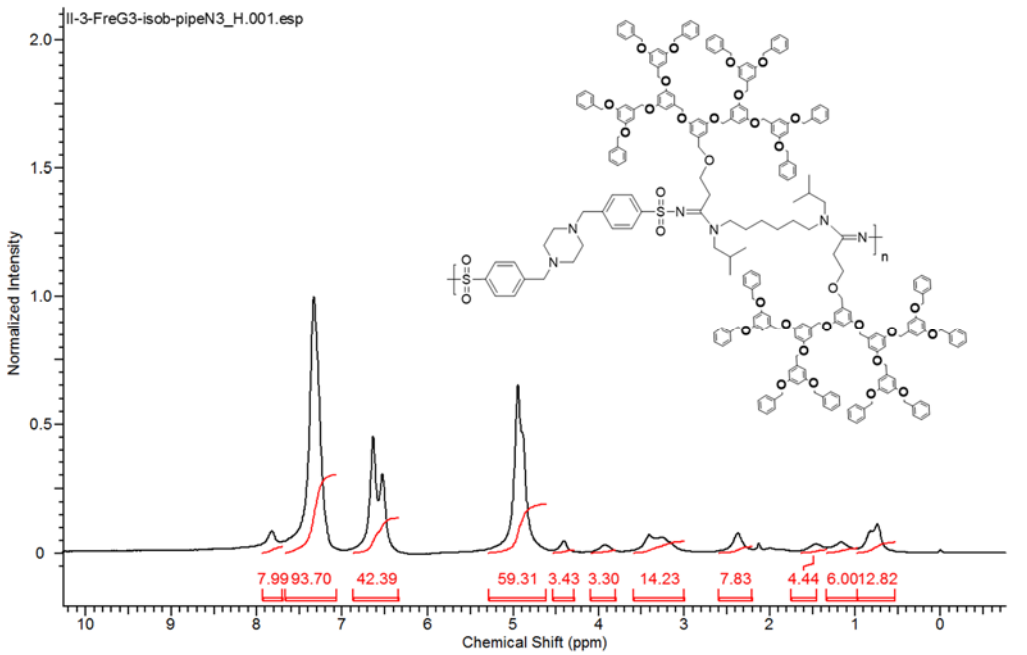


Table Ⅲ-4, entry 3 ($CDCl_3$)



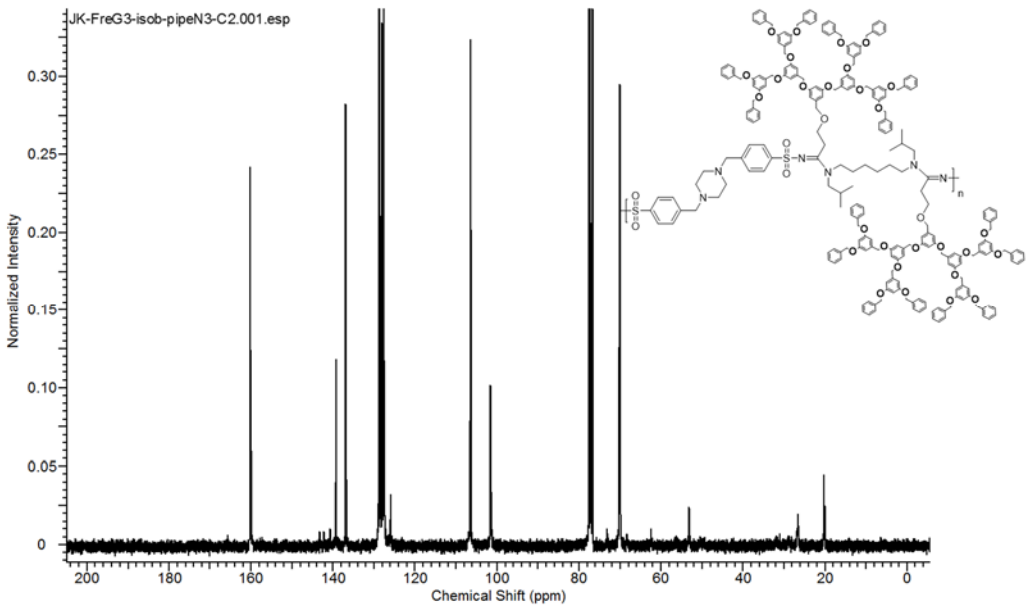
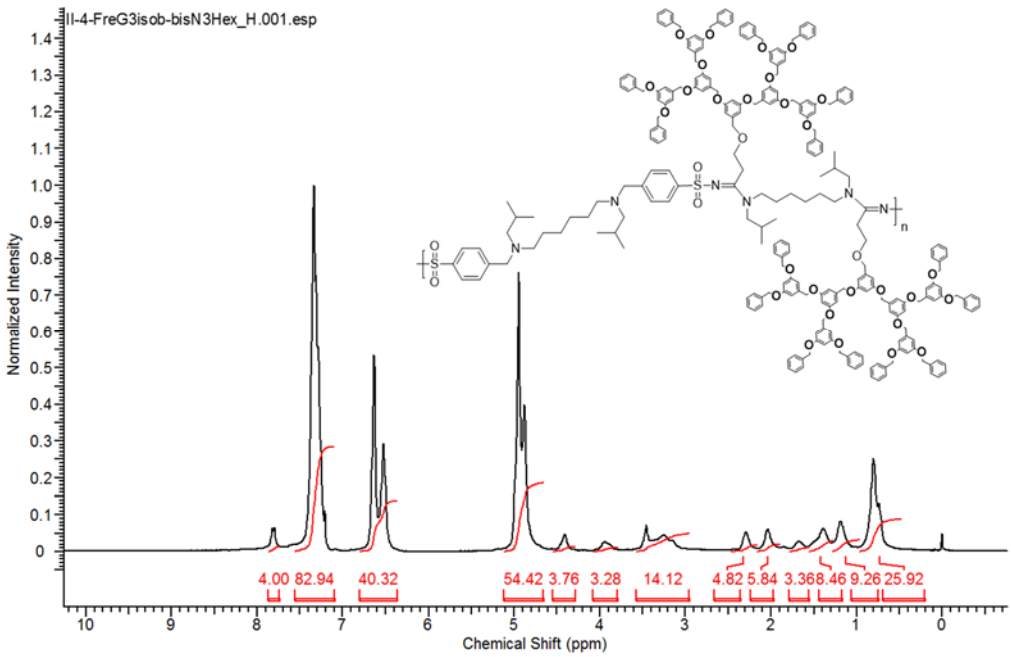


Table Ⅲ-4, entry 4 ($CDCl_3$)



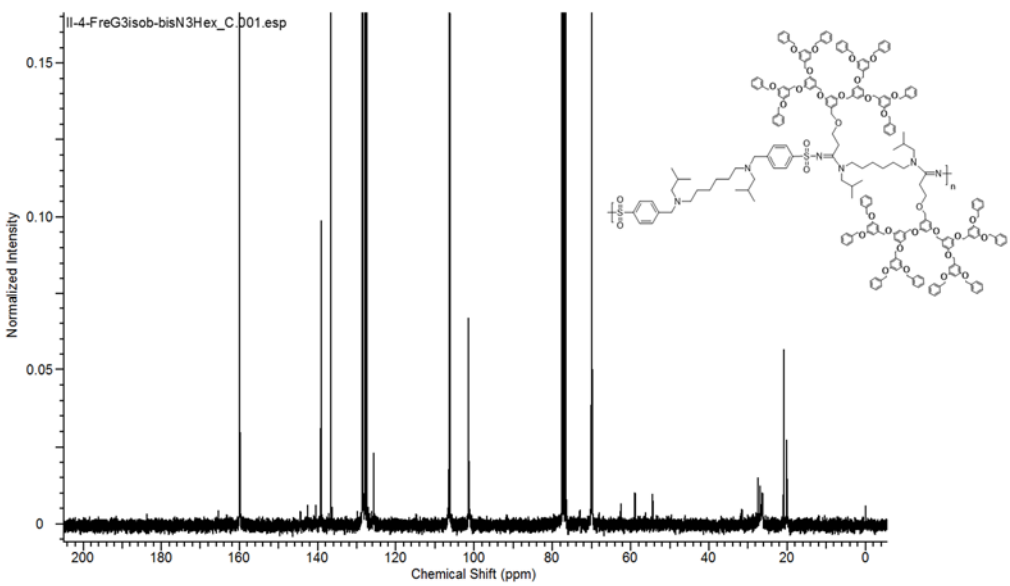
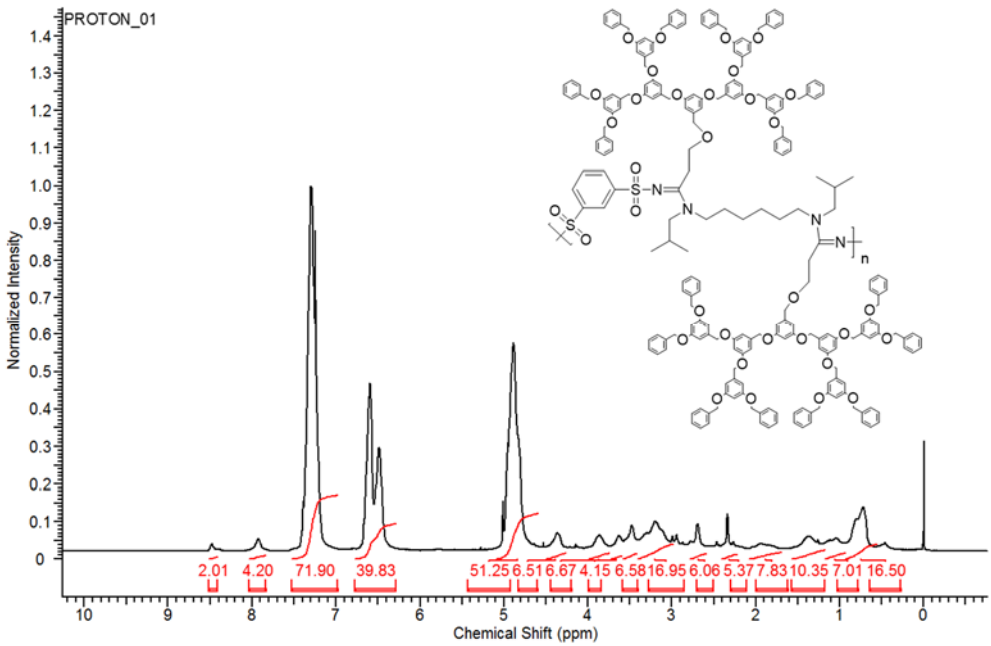


Table Ⅲ-4, entry 5 ($CDCl_3$)



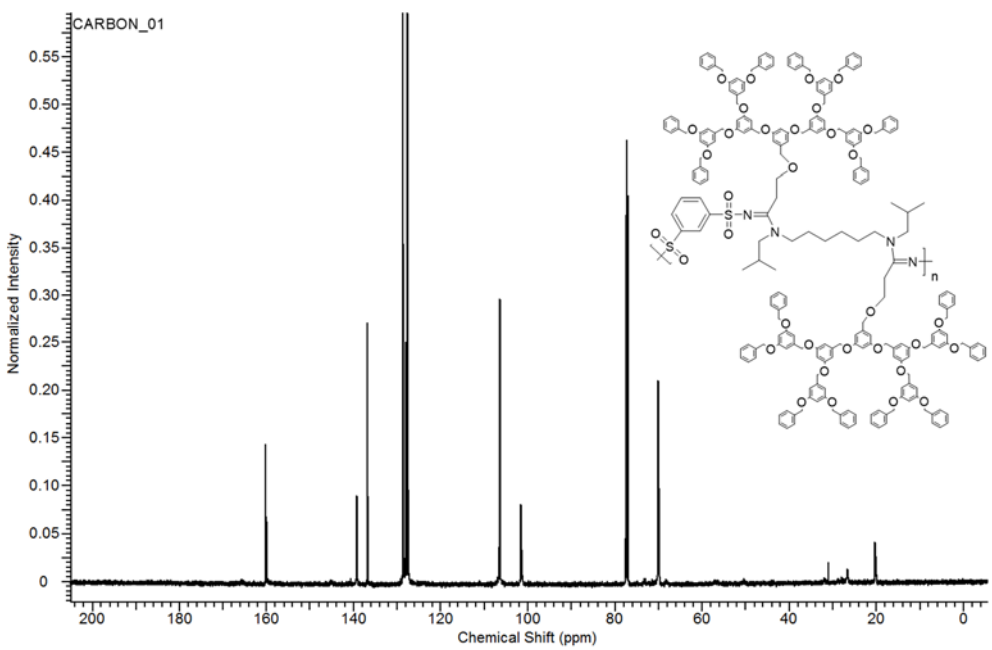
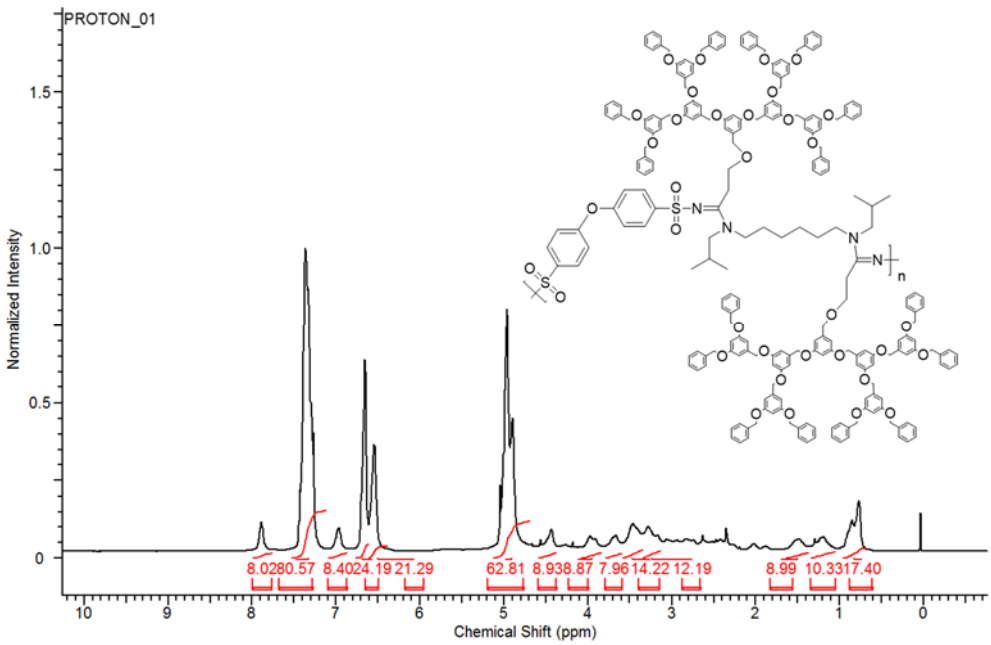


Table Ⅲ-4, entry 6 ($CDCl_3$)



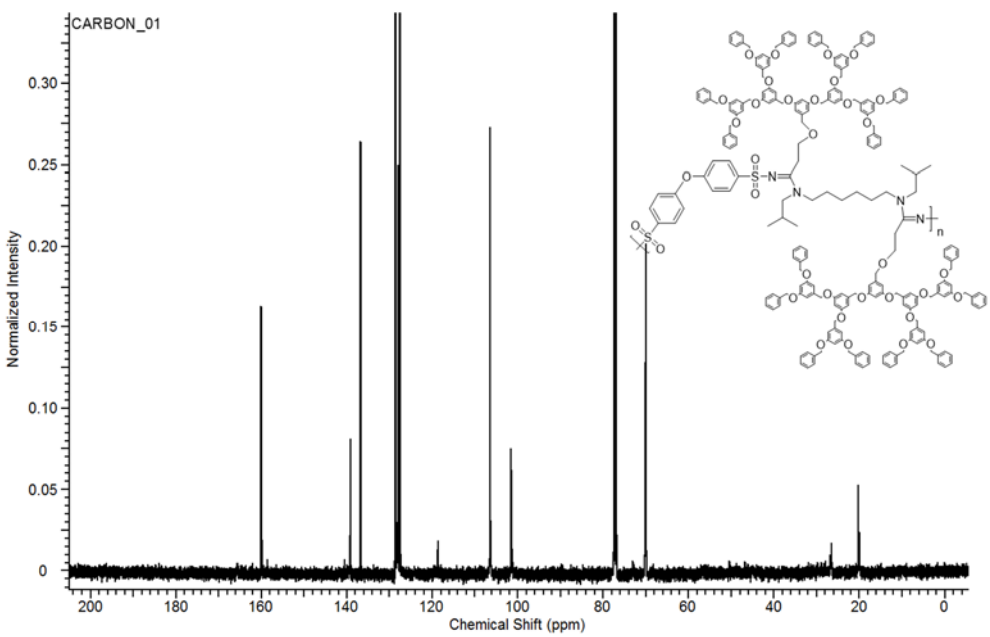
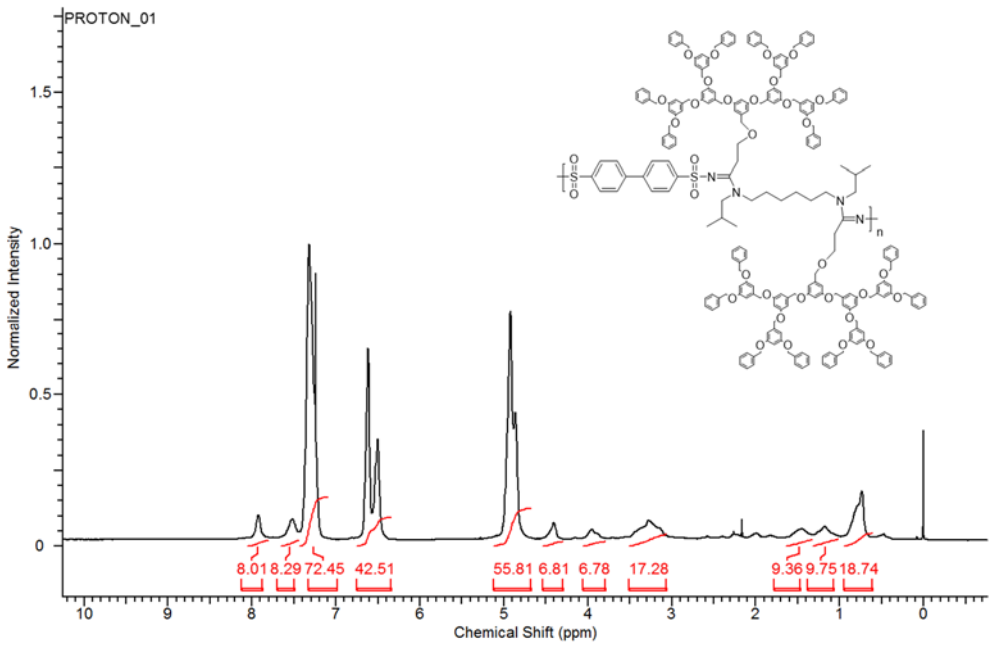


Table Ⅲ-4, entry 7 ($CDCl_3$)



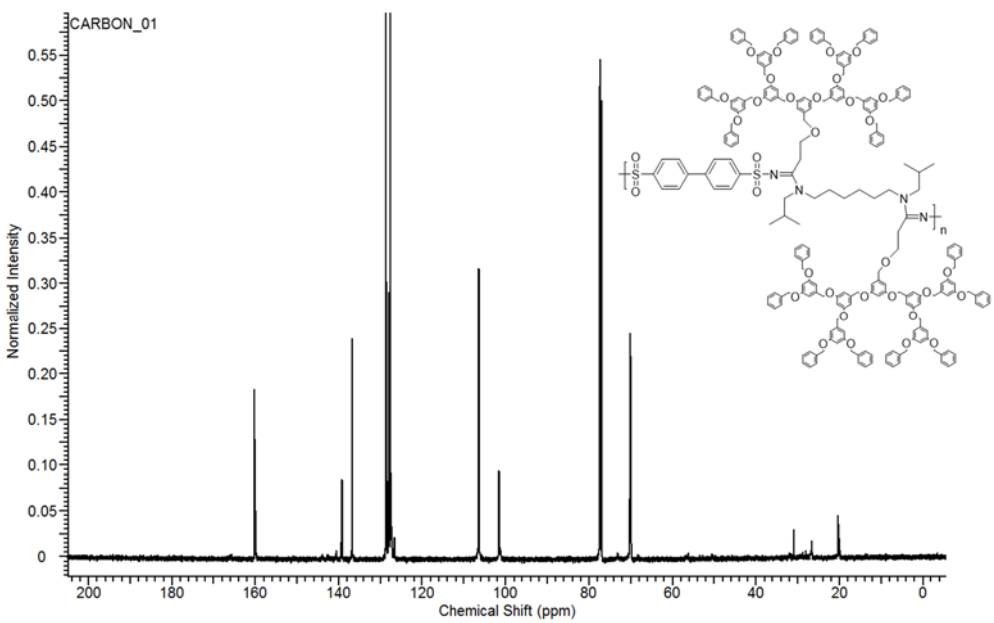
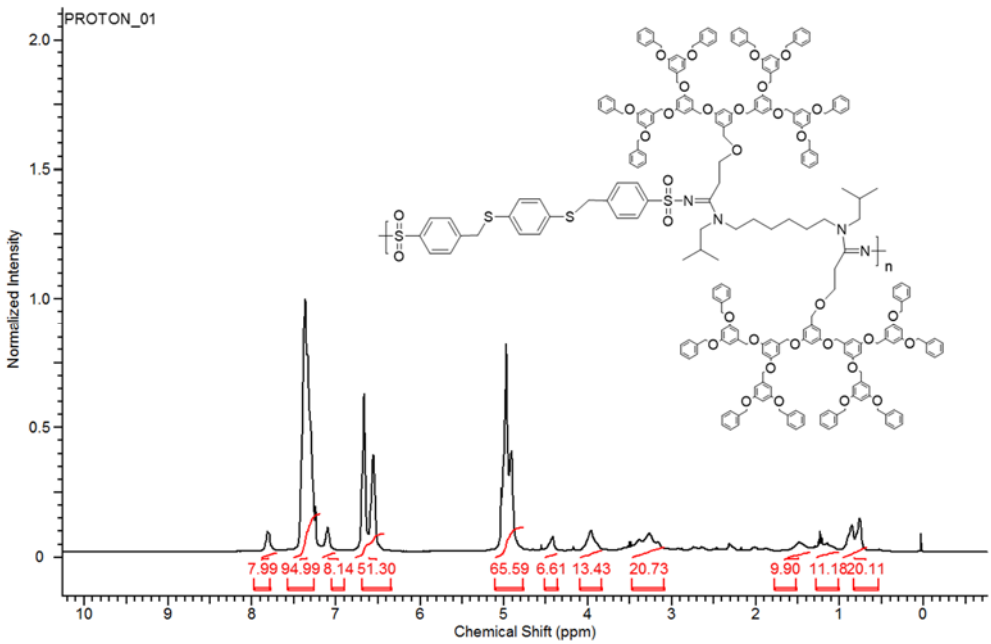


Table Ⅲ-4, entry 8 ($CDCl_3$)



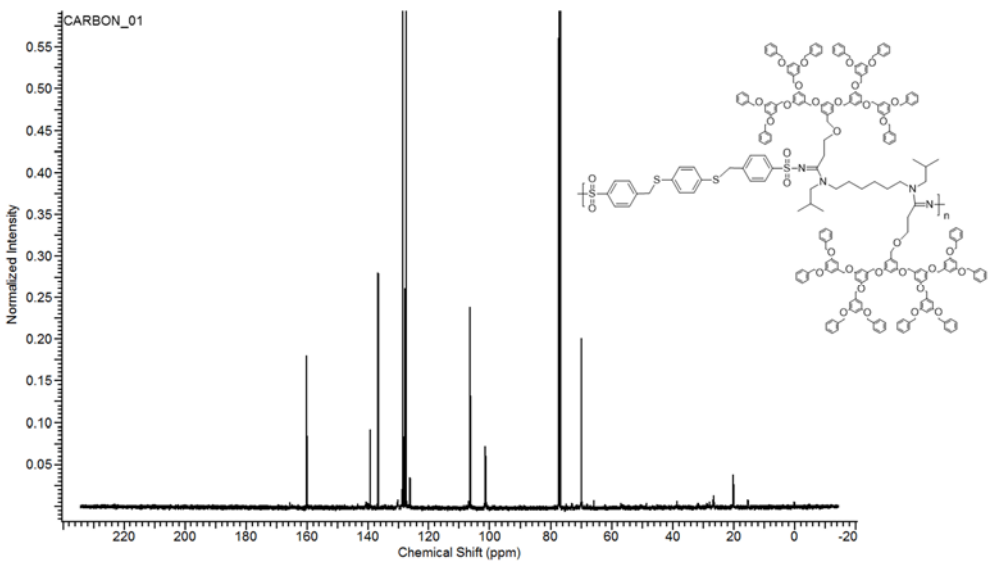


Table Ⅲ-4, entry 9 ($CDCl_3$)

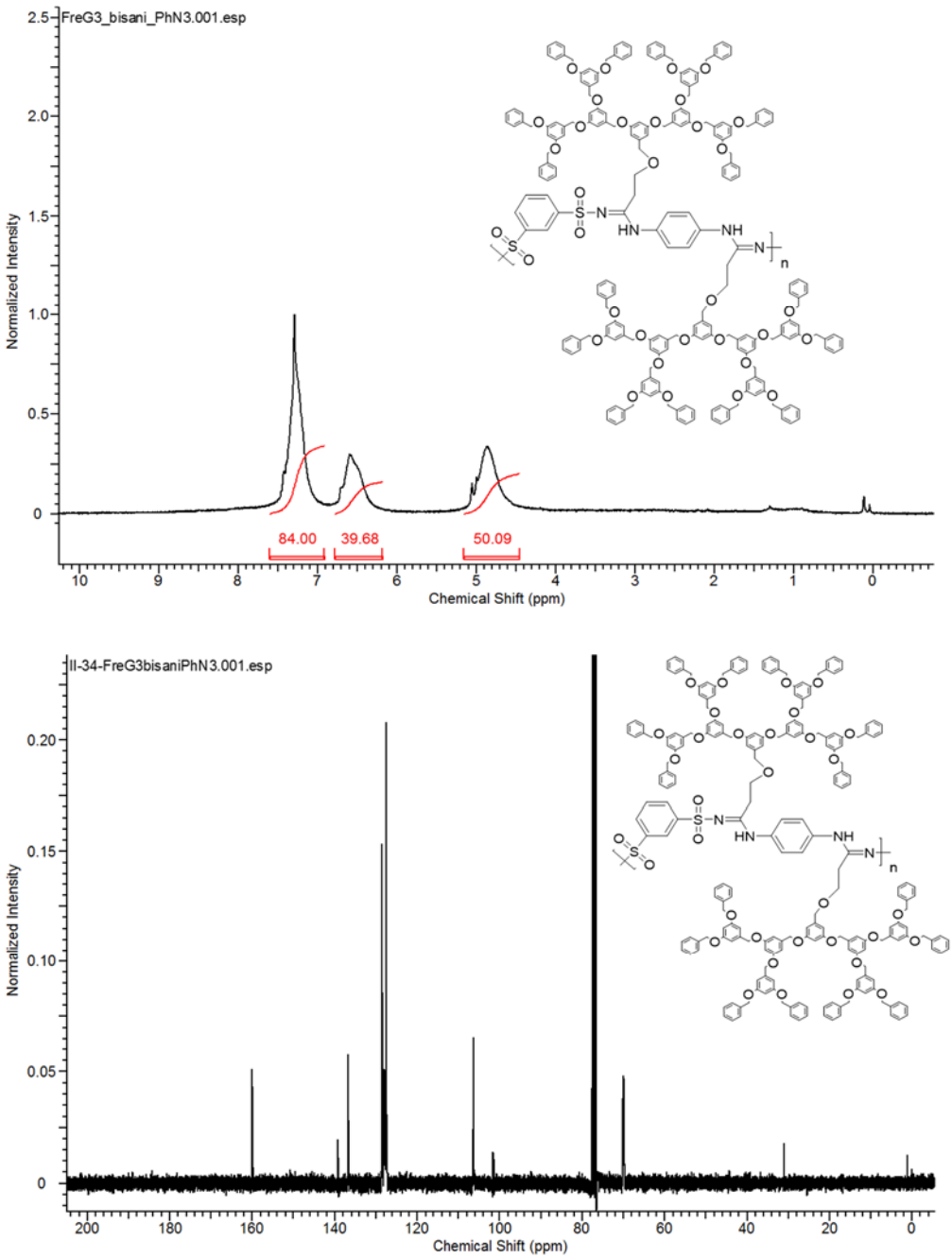
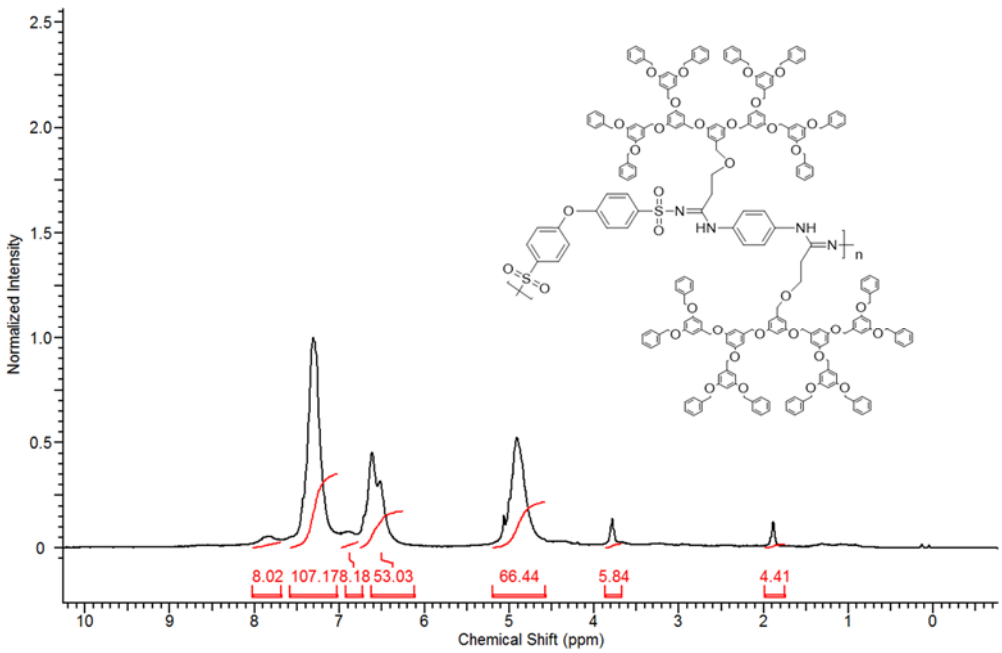


Table Ⅲ-4, entry 10 ($CDCl_3$)



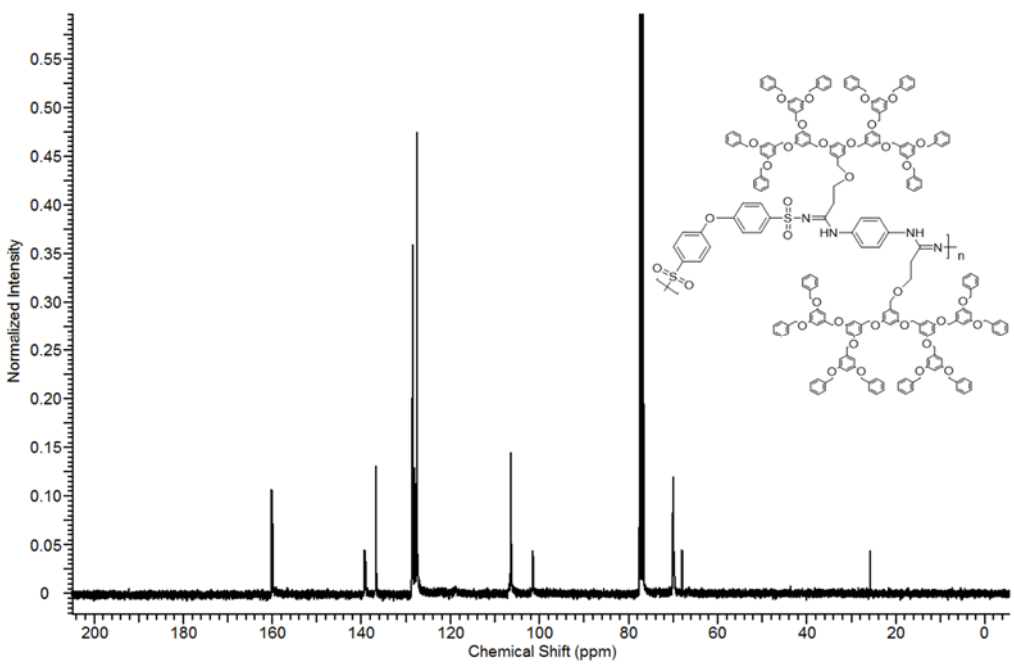
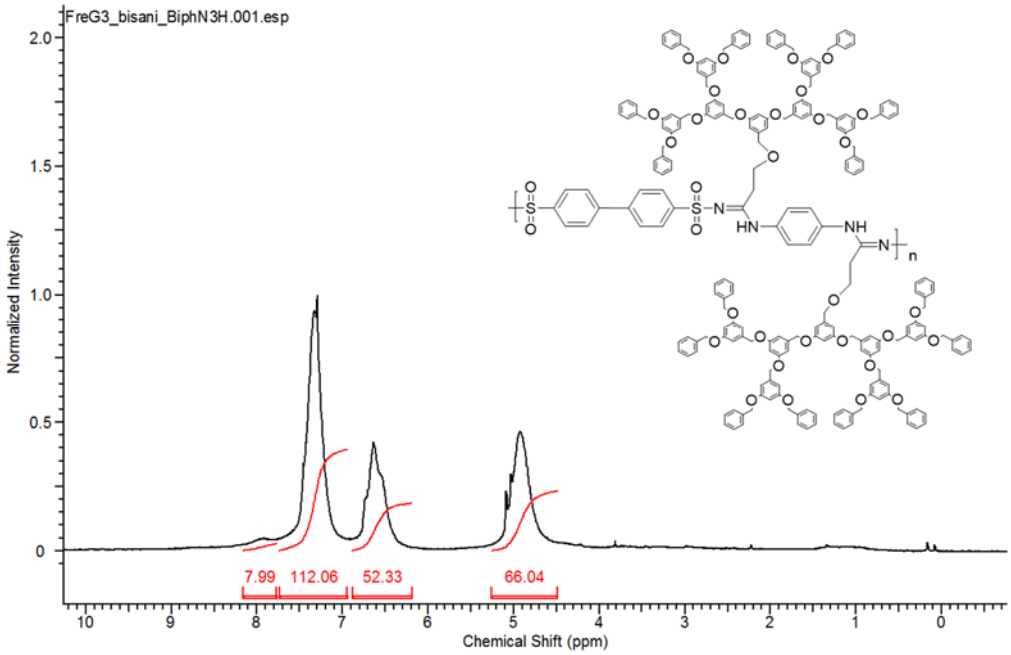
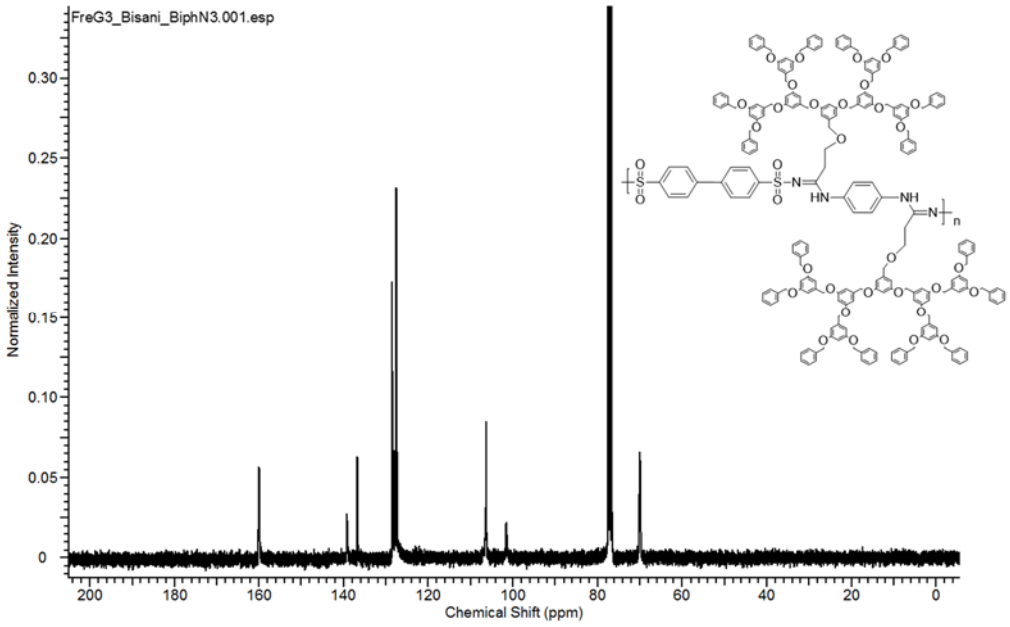


Table Ⅲ-4, entry 11 ($CDCl_3$)





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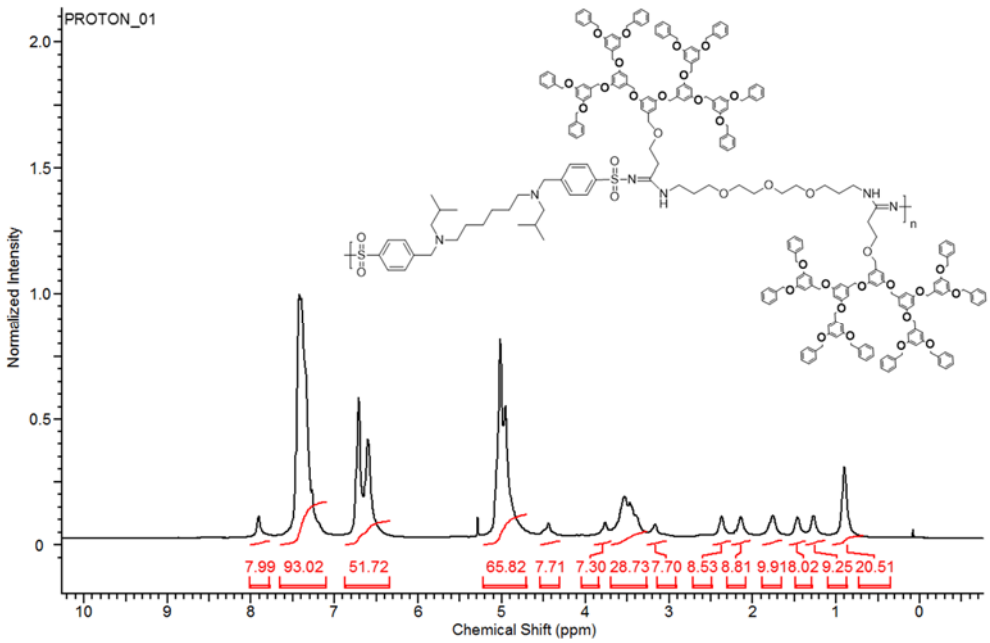


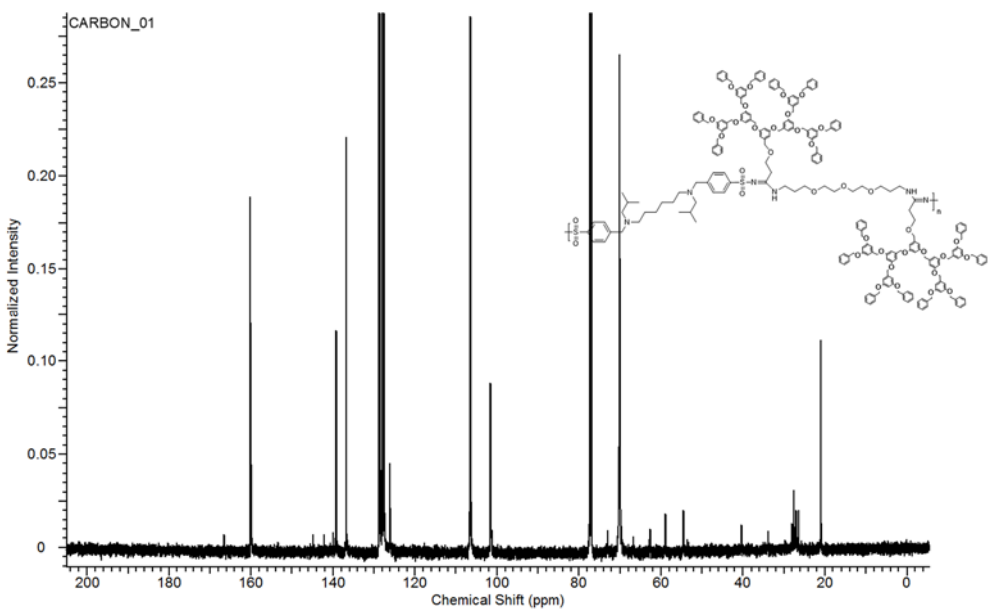
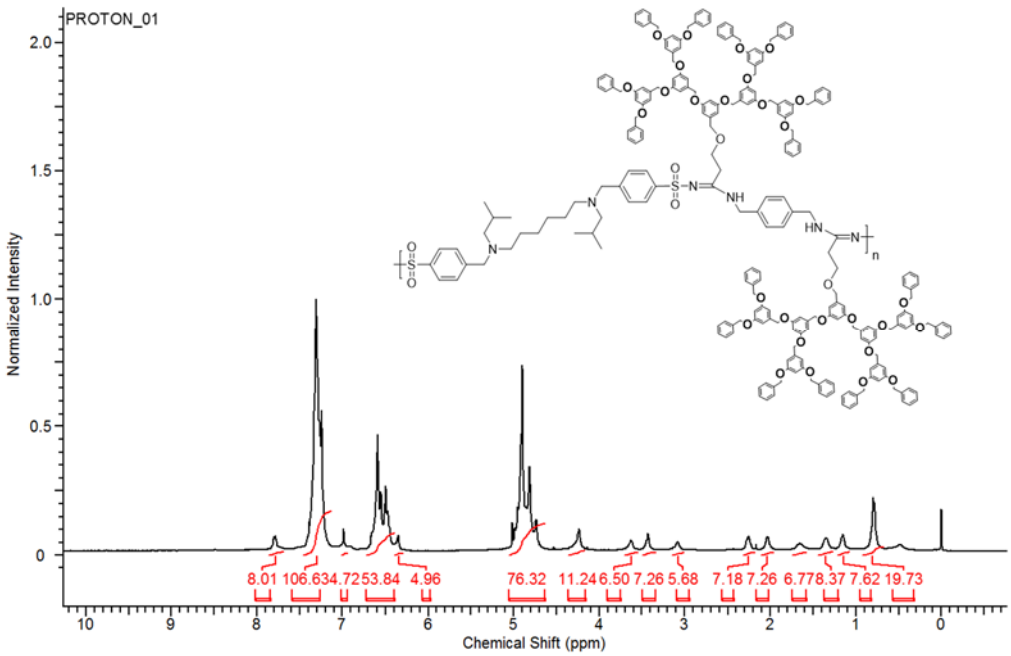


Table Ⅲ-4, entry 13 ($CDCl_3$)



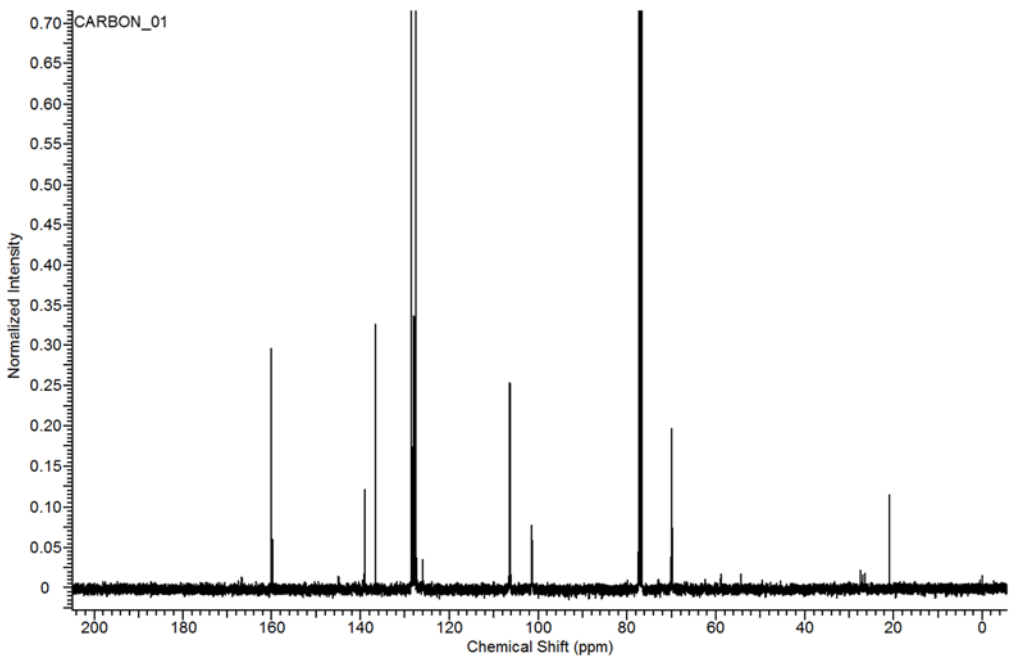
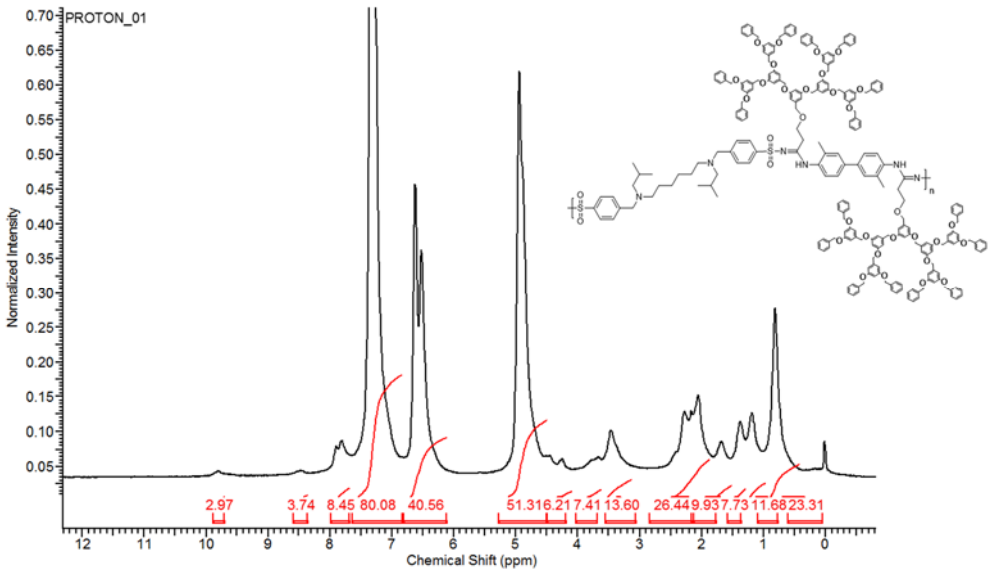


Table Ⅲ-4, entry 14 ($CDCl_3$)



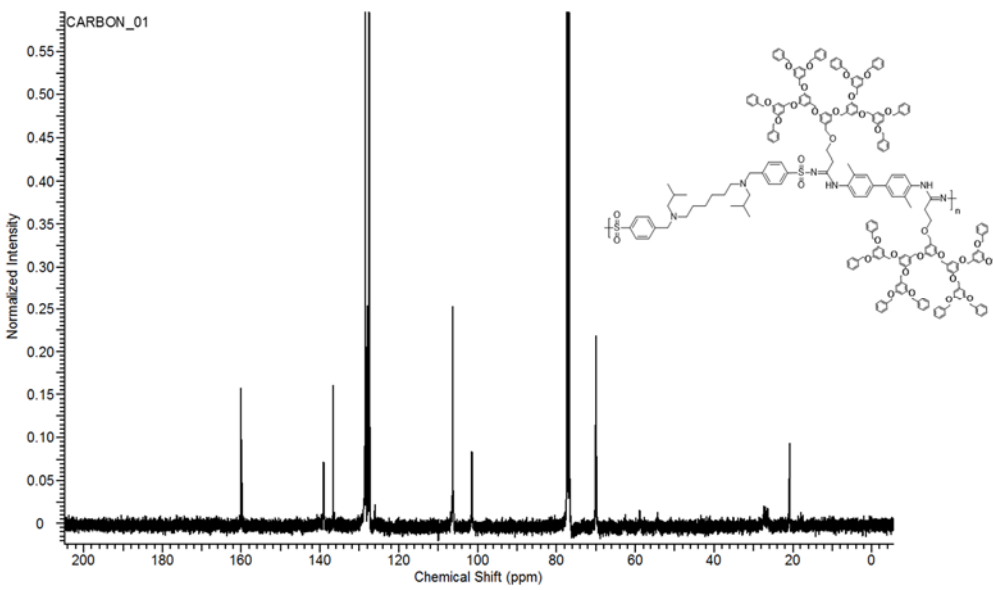
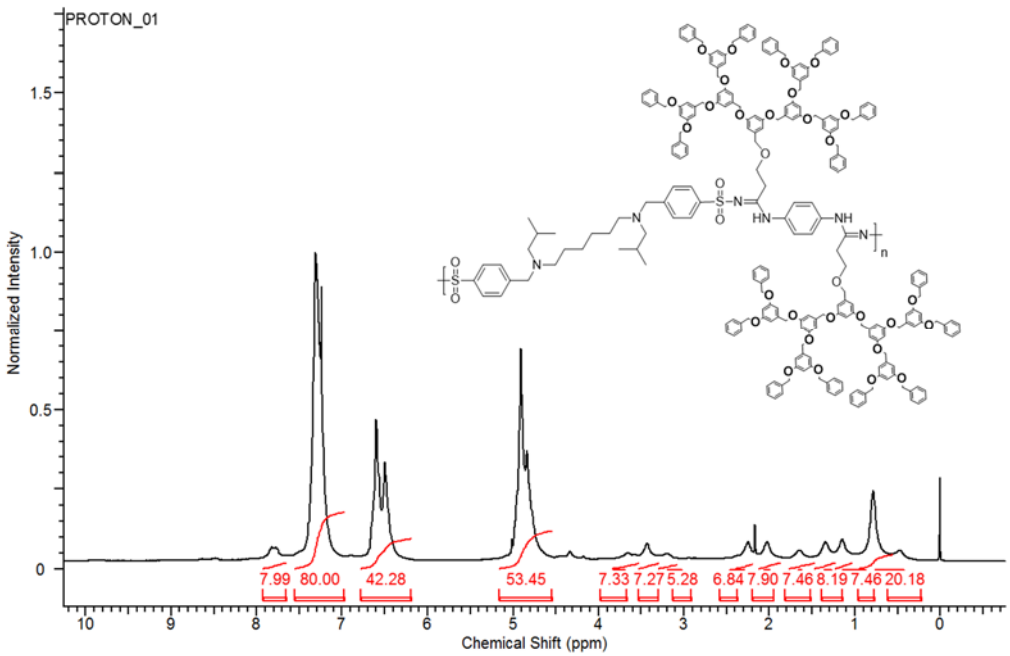


Table Ⅲ-4, entry 15 ($CDCl_3$)



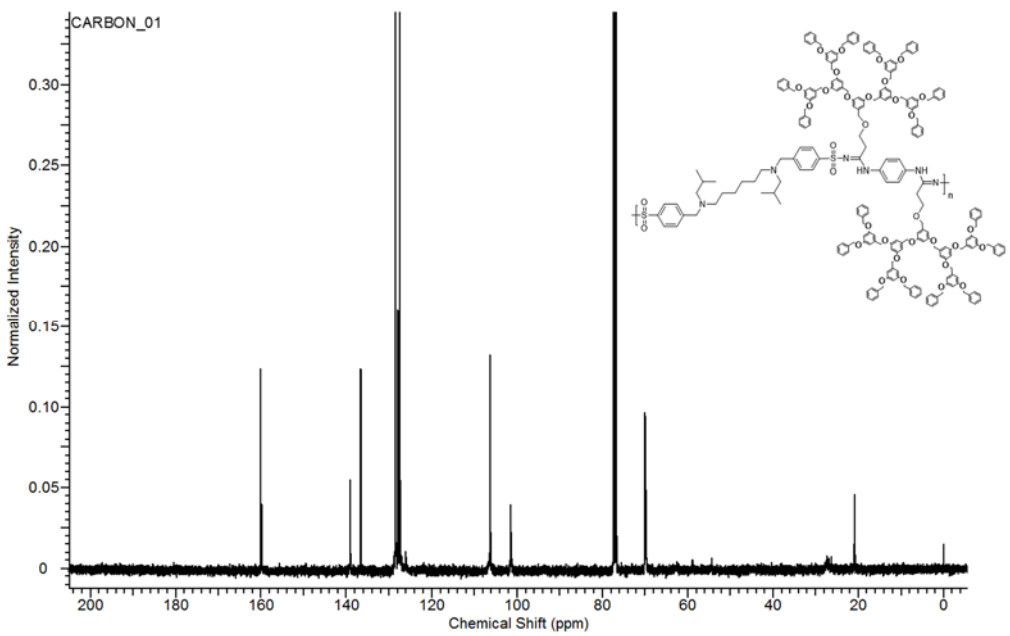
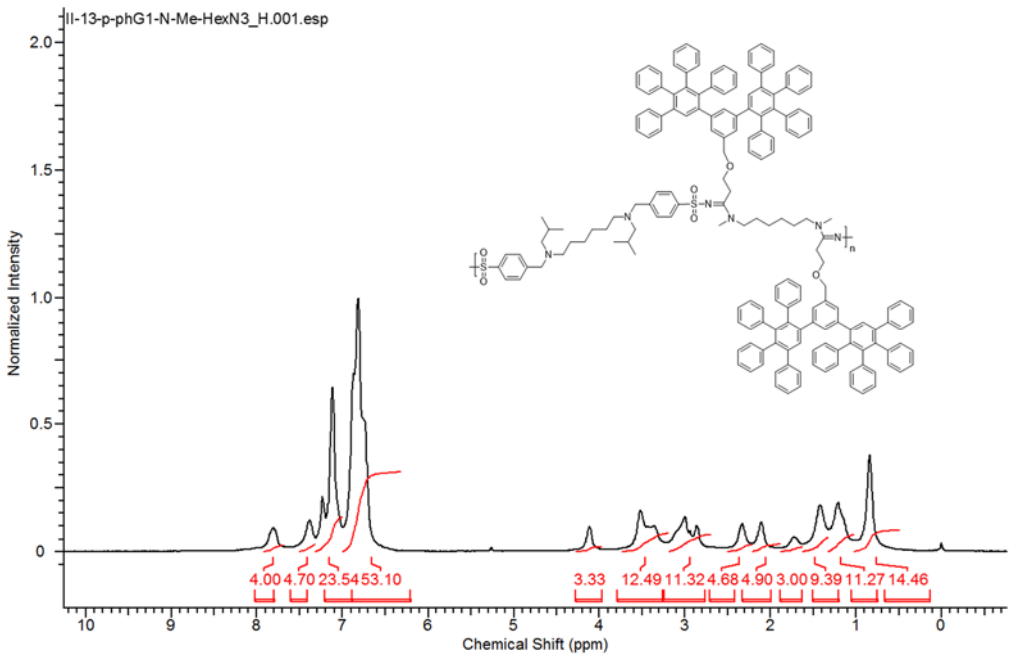


Table Ⅲ-4, entry 16 ($CDCl_3$)



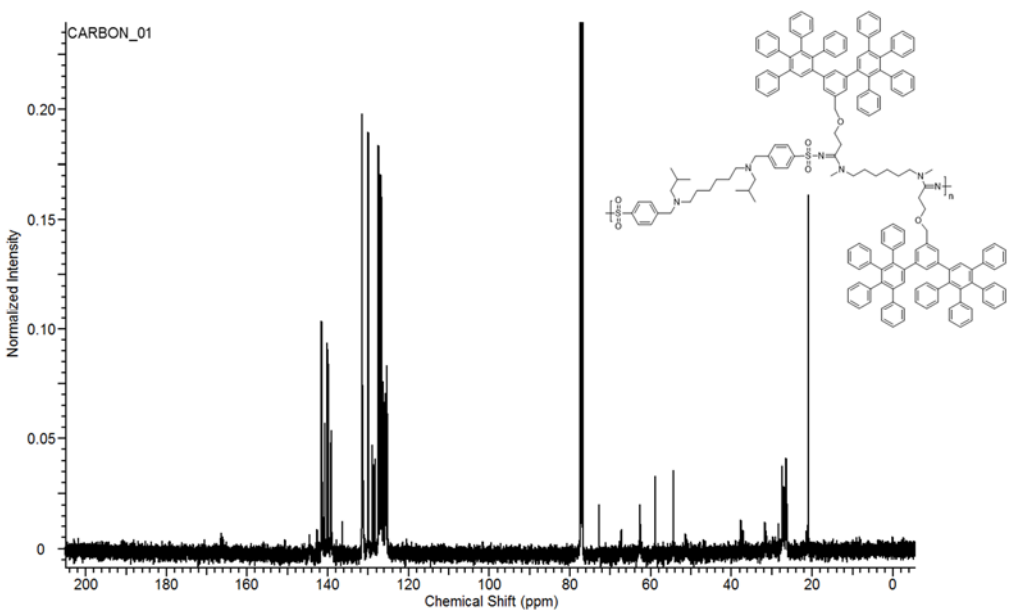
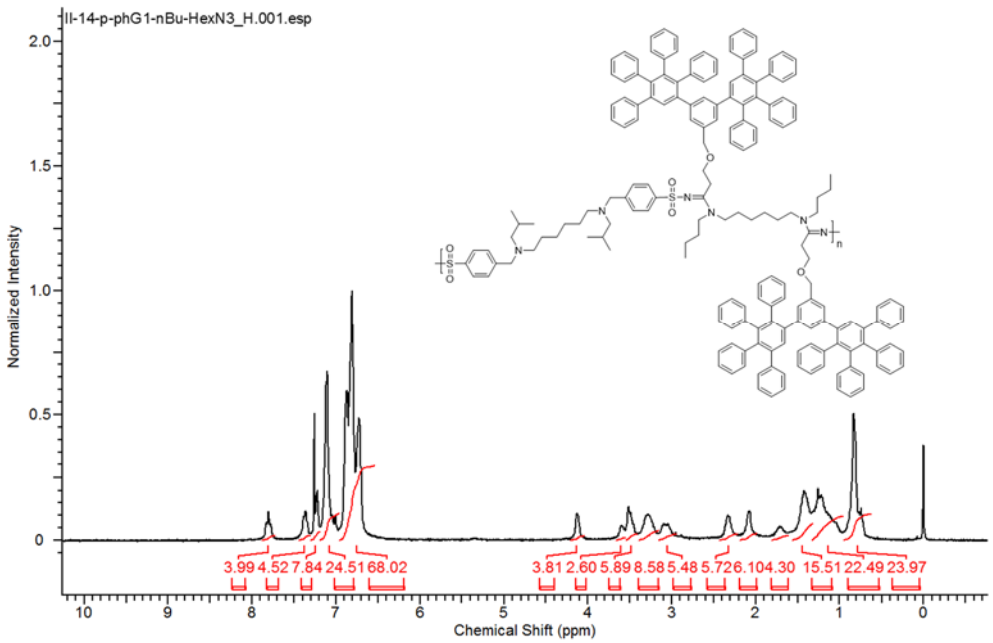


Table Ⅲ-4, entry 17 ($CDCl_3$)



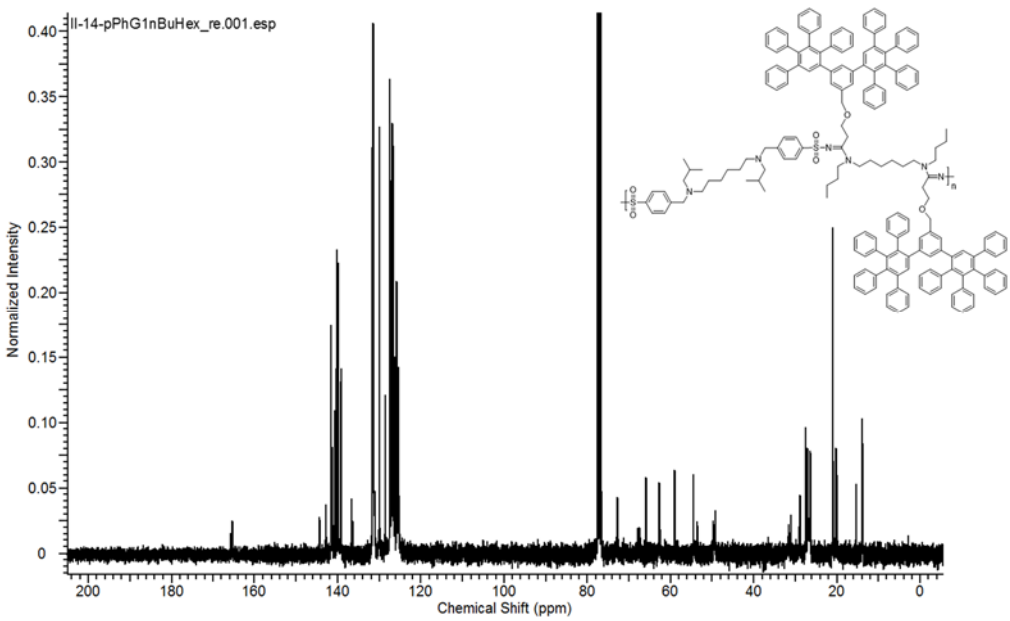
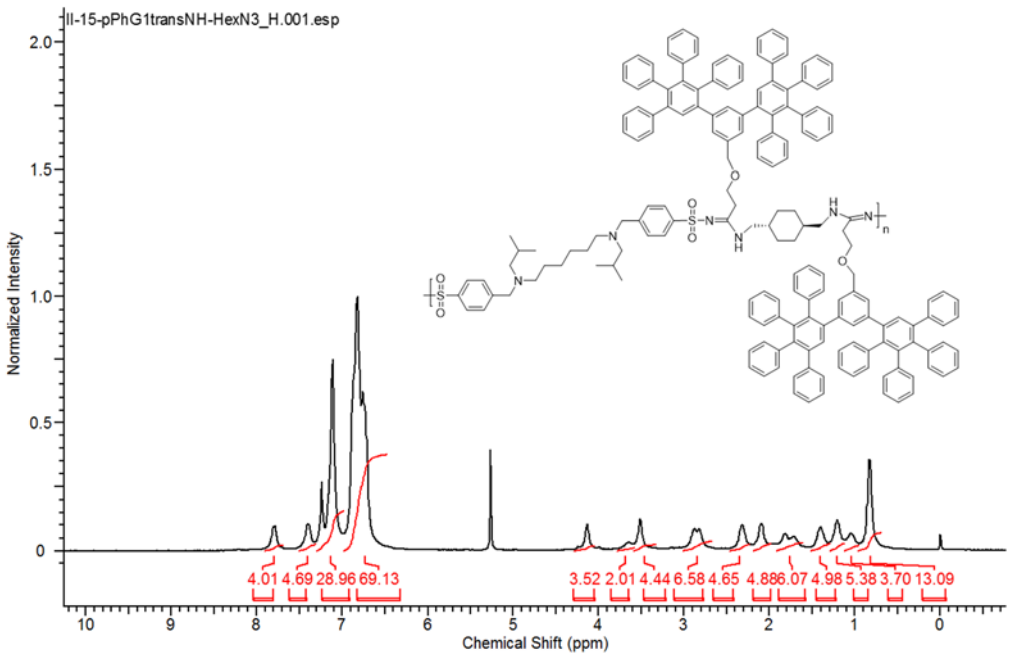


Table Ⅲ-4, entry 18 ($CDCl_3$)



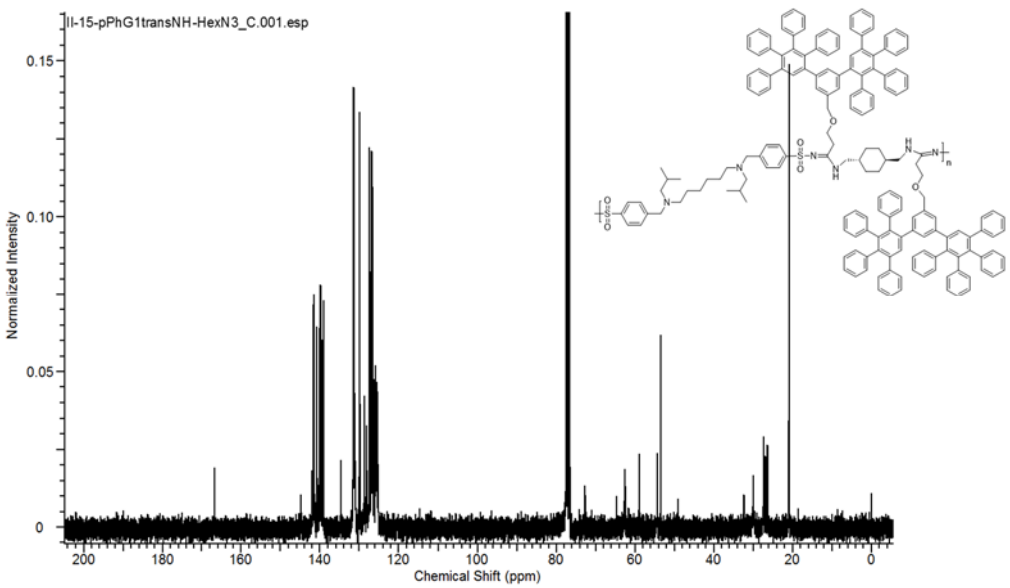
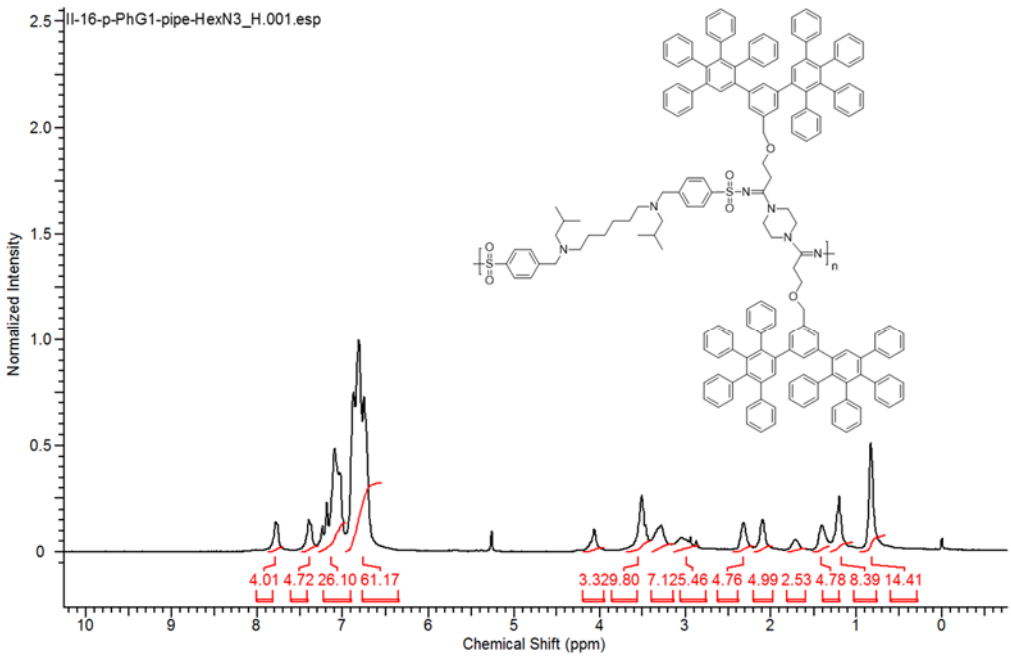
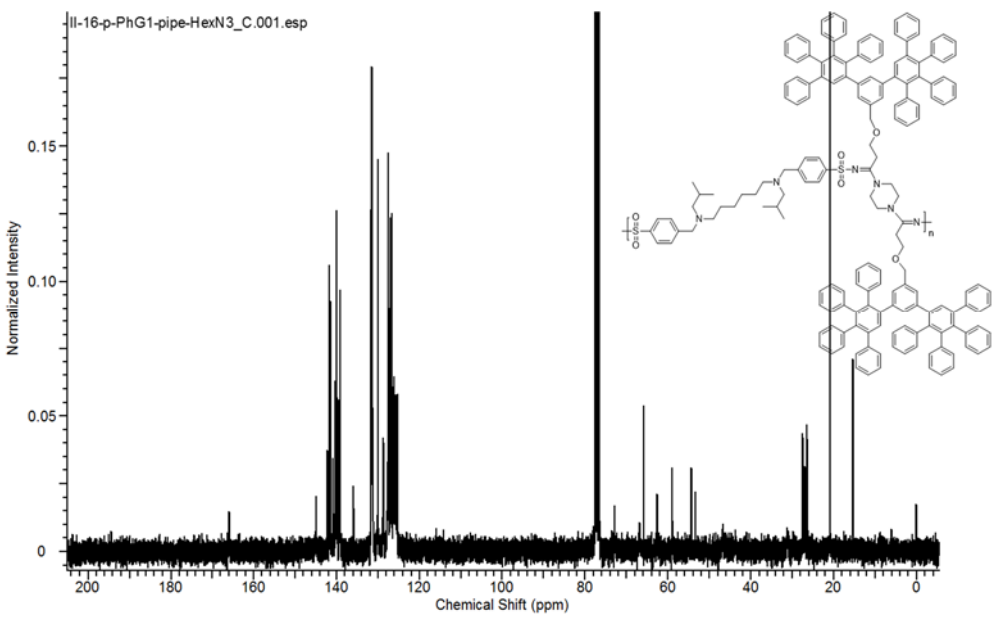


Table Ⅲ-4, entry 19 ($CDCl_3$)





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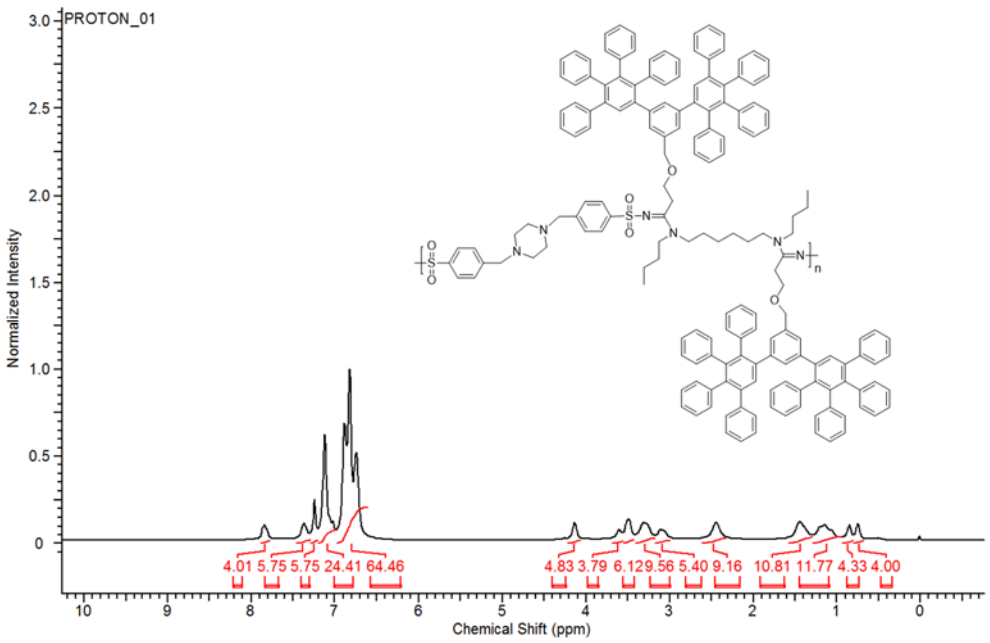


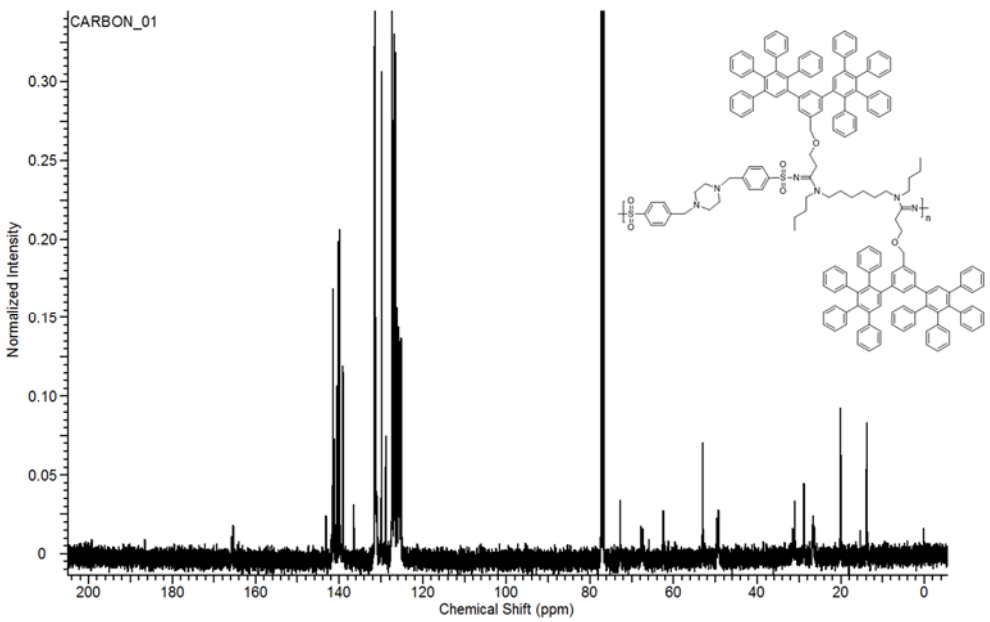
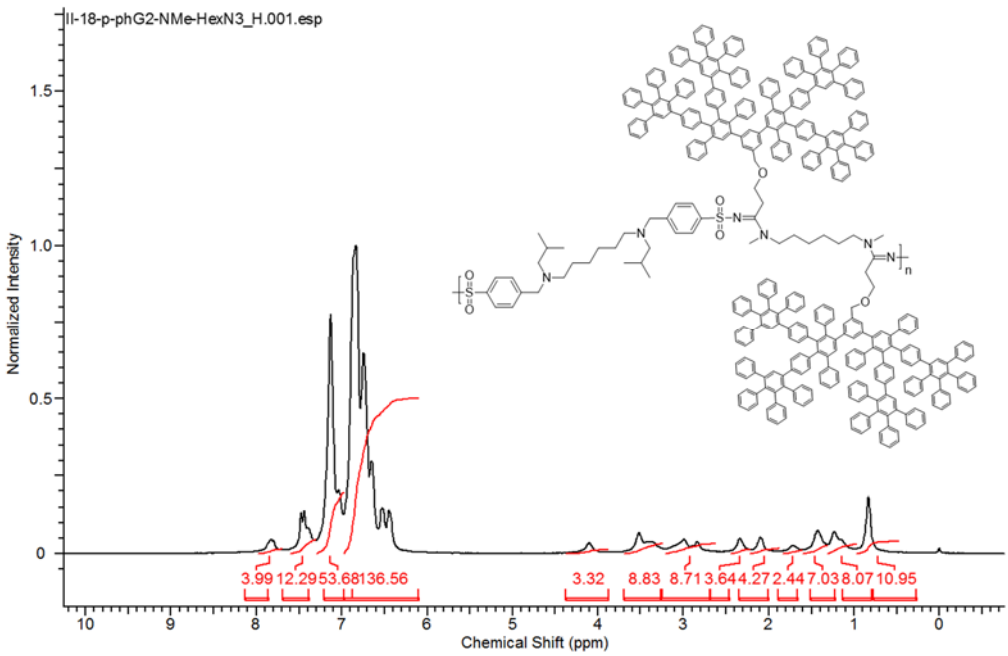


Table Ⅲ-4, entry 21 ($CDCl_3$)



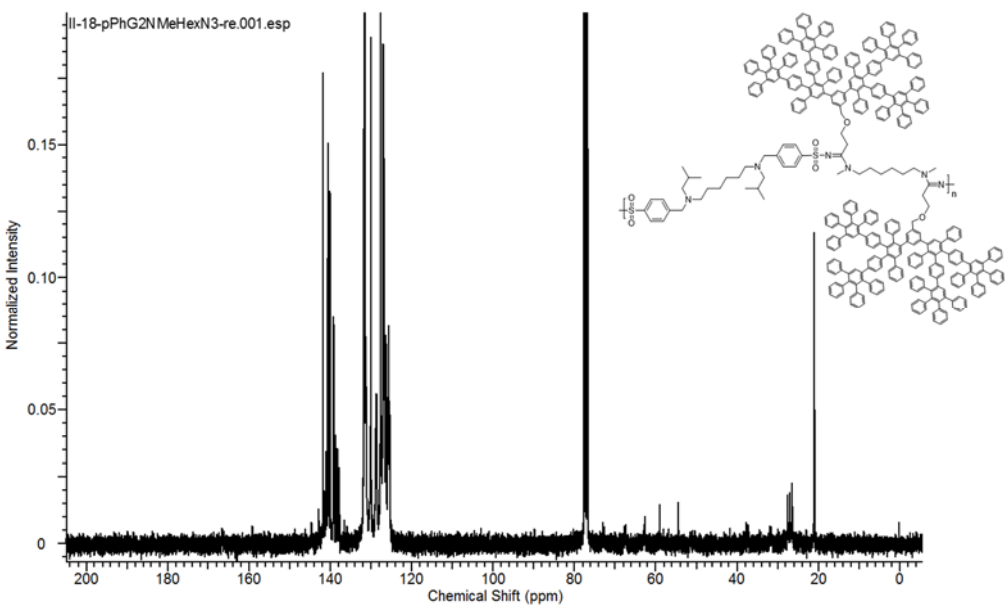
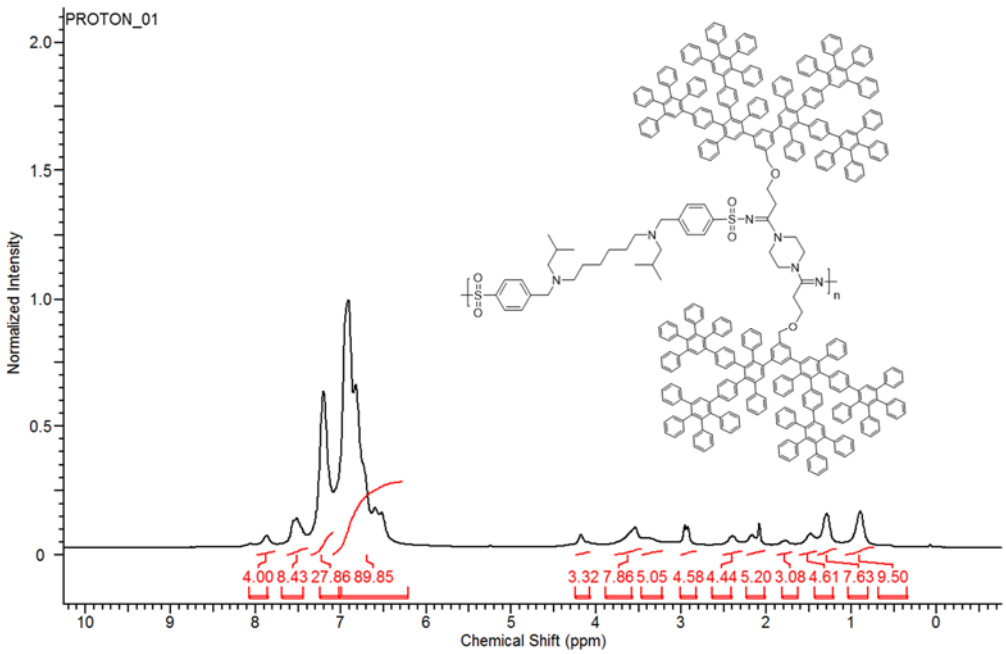


Table Ⅲ-4, entry 22 ($CDCl_3$)



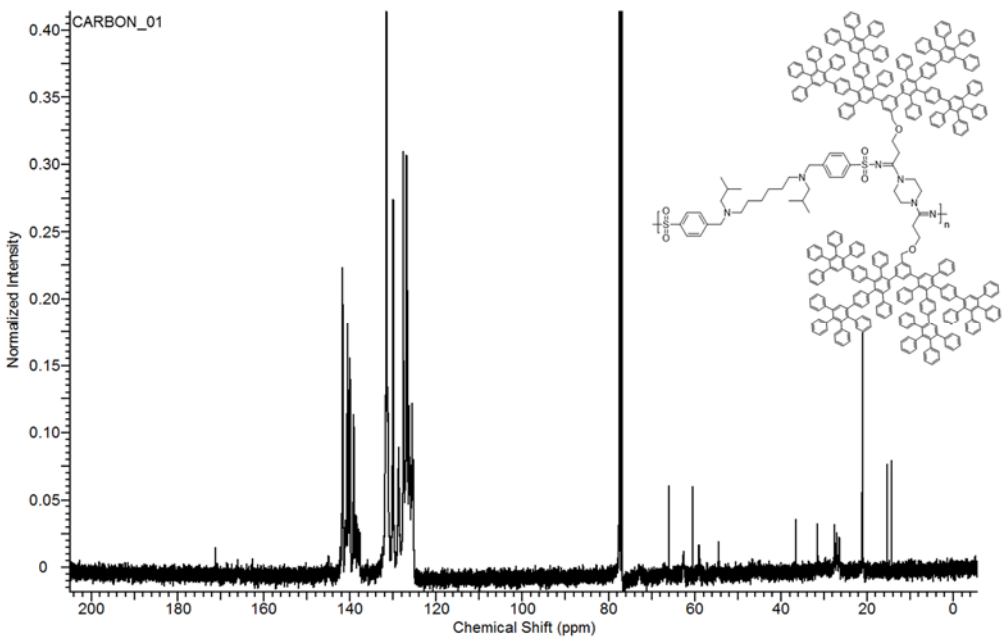
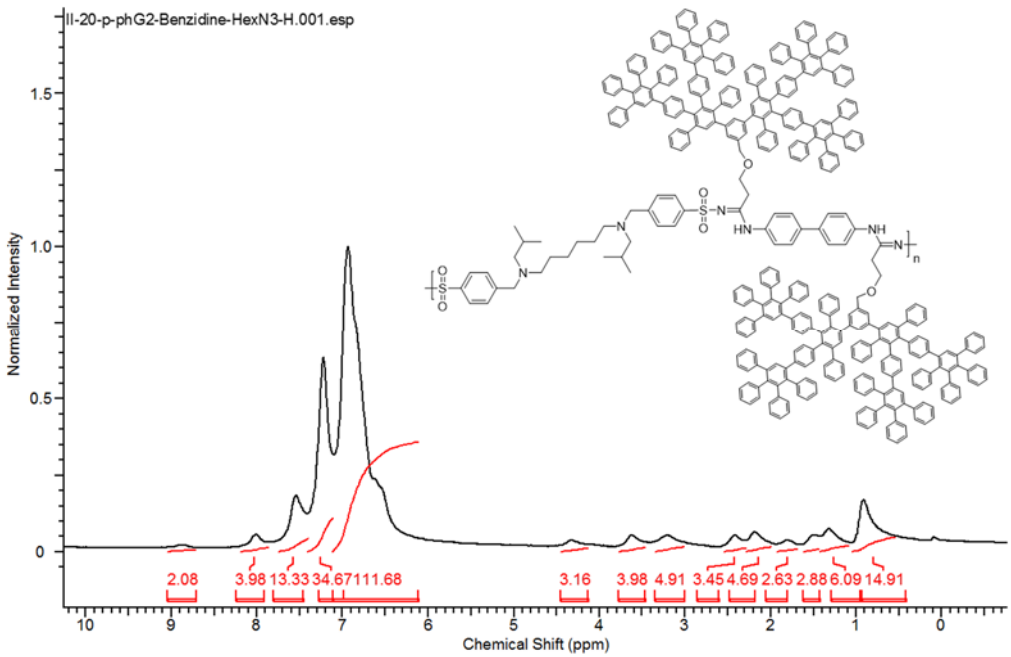


Table Ⅲ-4, entry 23 ($CDCl_3$)



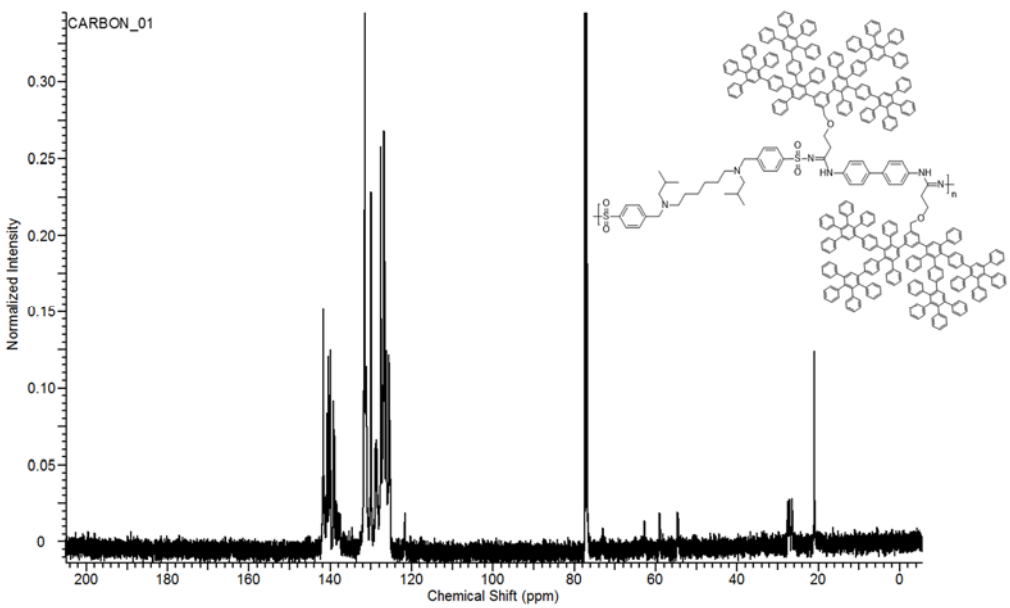
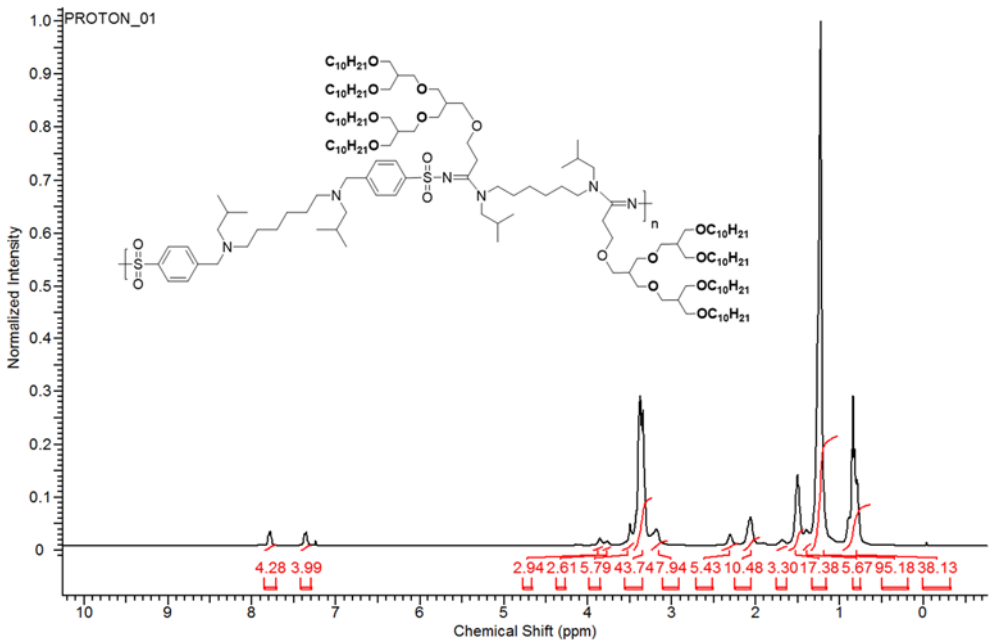


Table Ⅲ-4, entry 24 ($CDCl_3$)



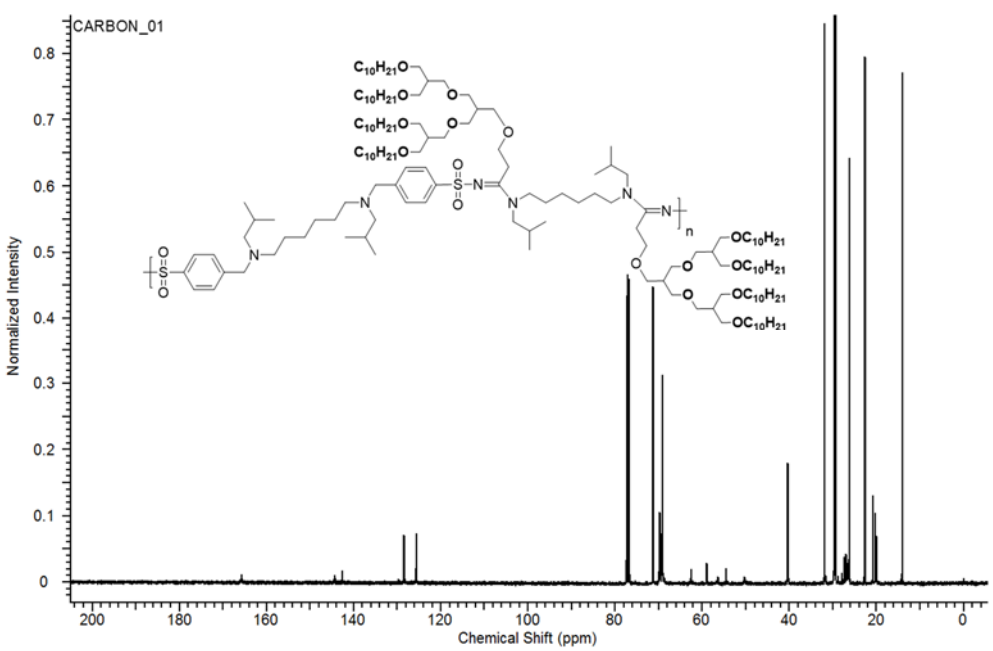
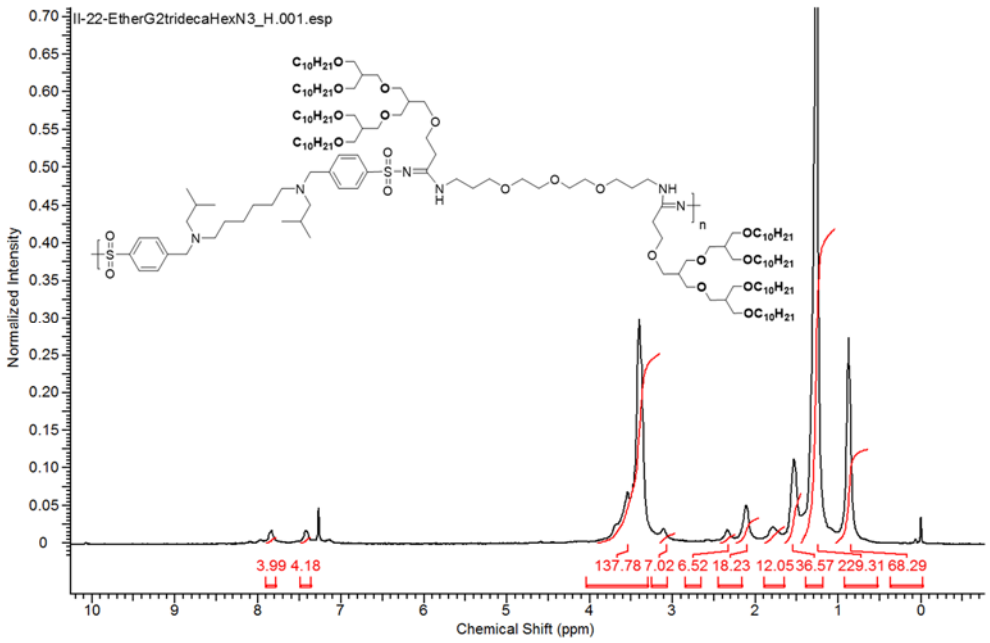


Table Ⅲ-4, entry 25 ($CDCl_3$)



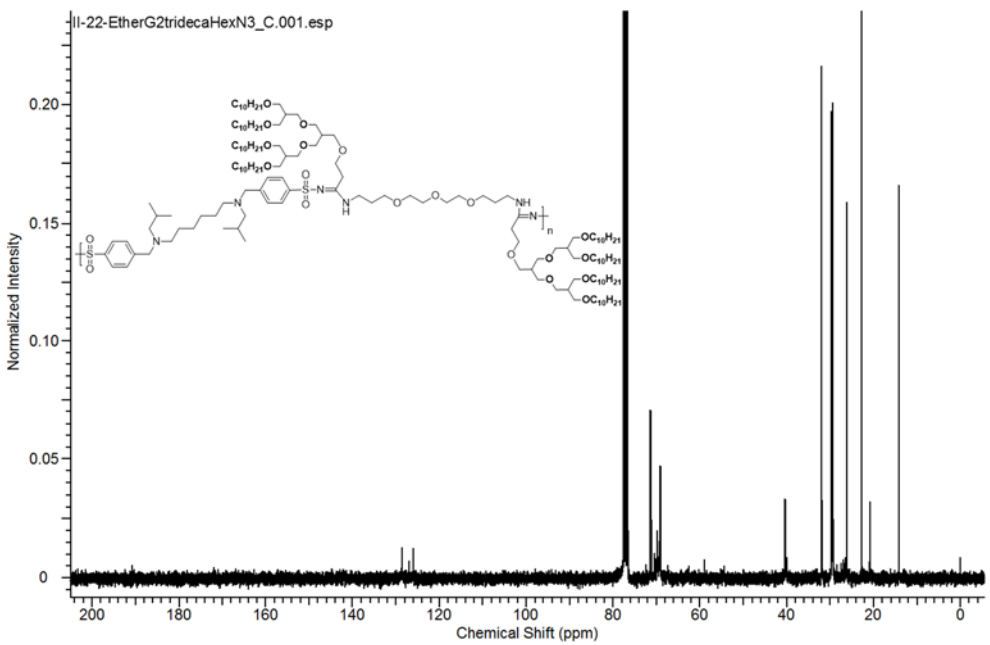
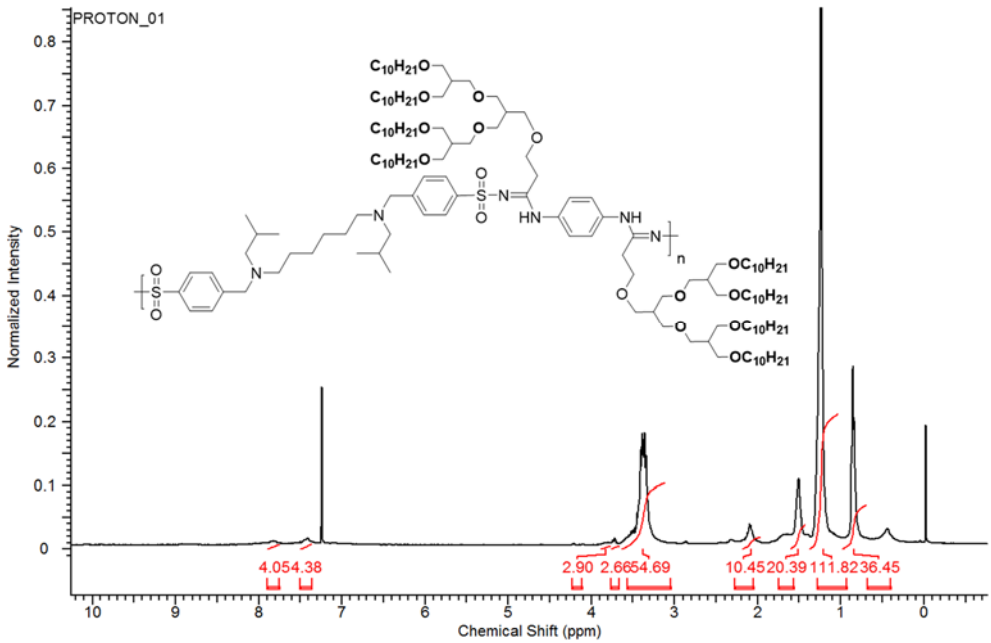


Table Ⅲ-4, entry 26 ($CDCl_3$)



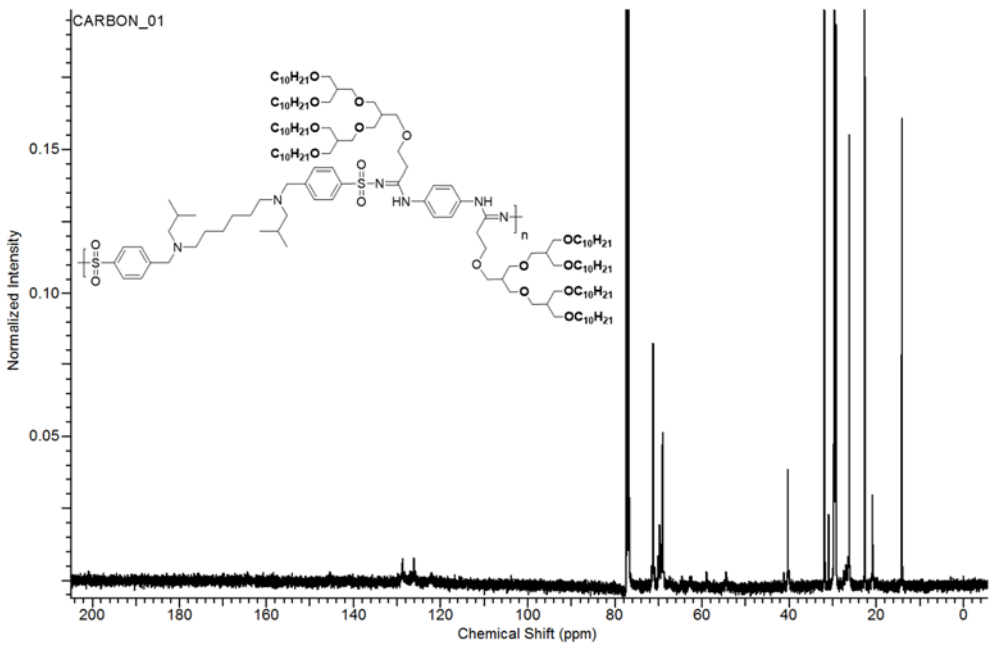
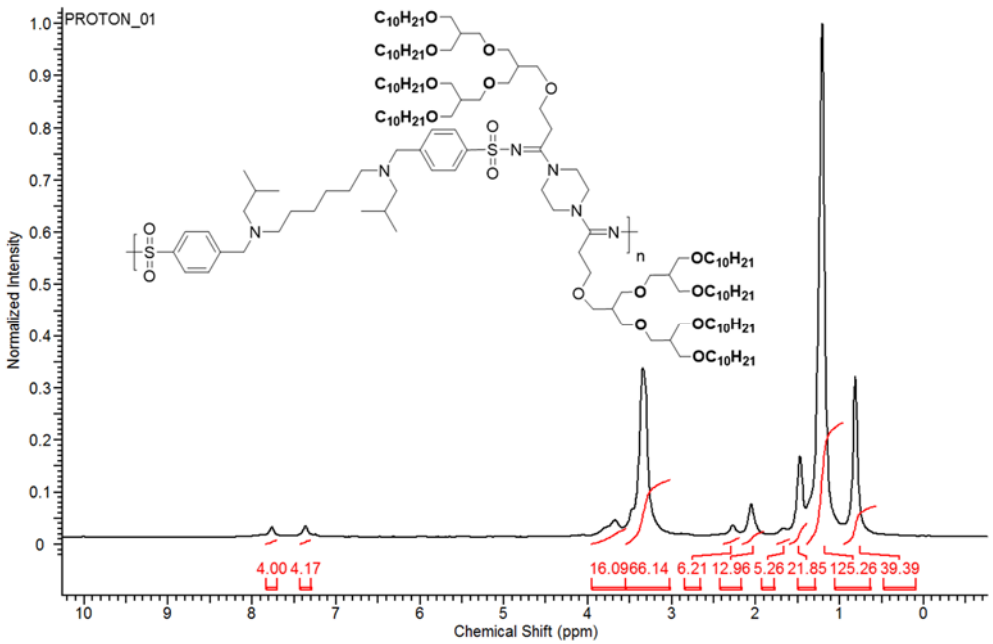


Table Ⅲ-4, entry 27 ($CDCl_3$)



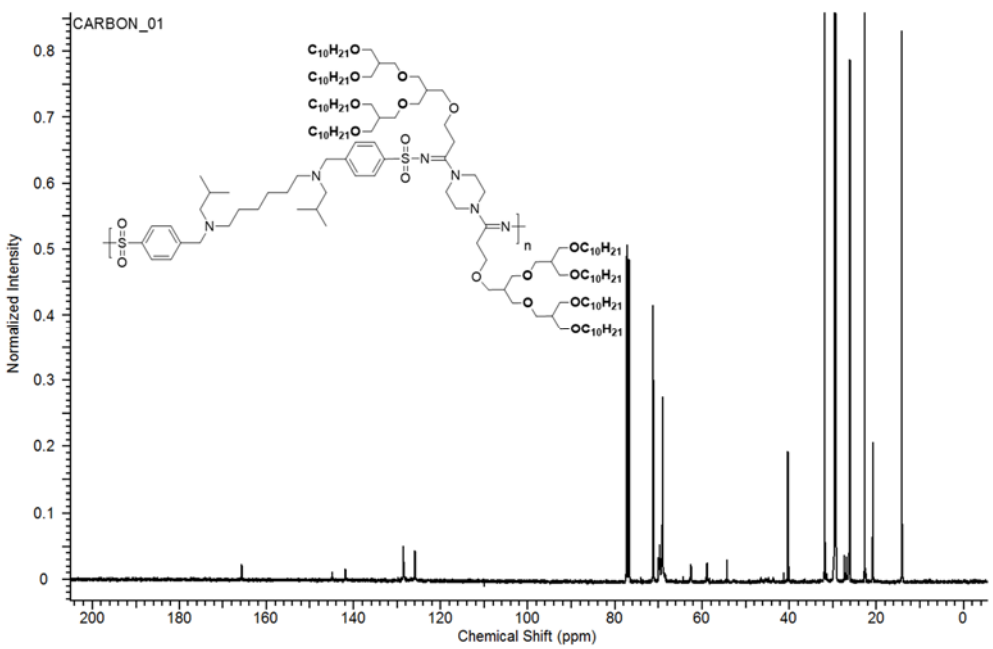
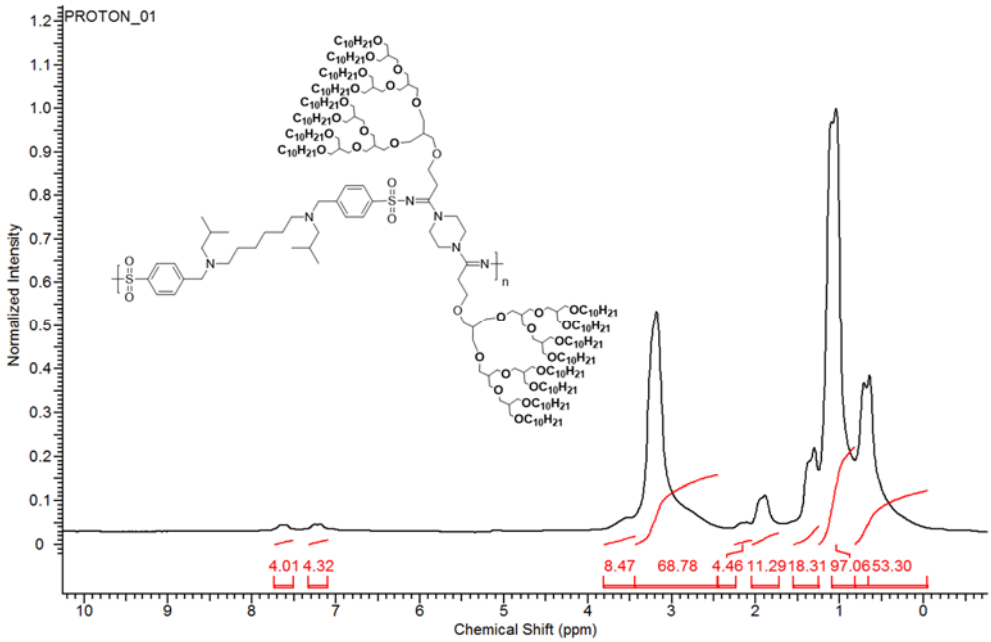


Table Ⅲ-4, entry 28 ($CDCl_3$)



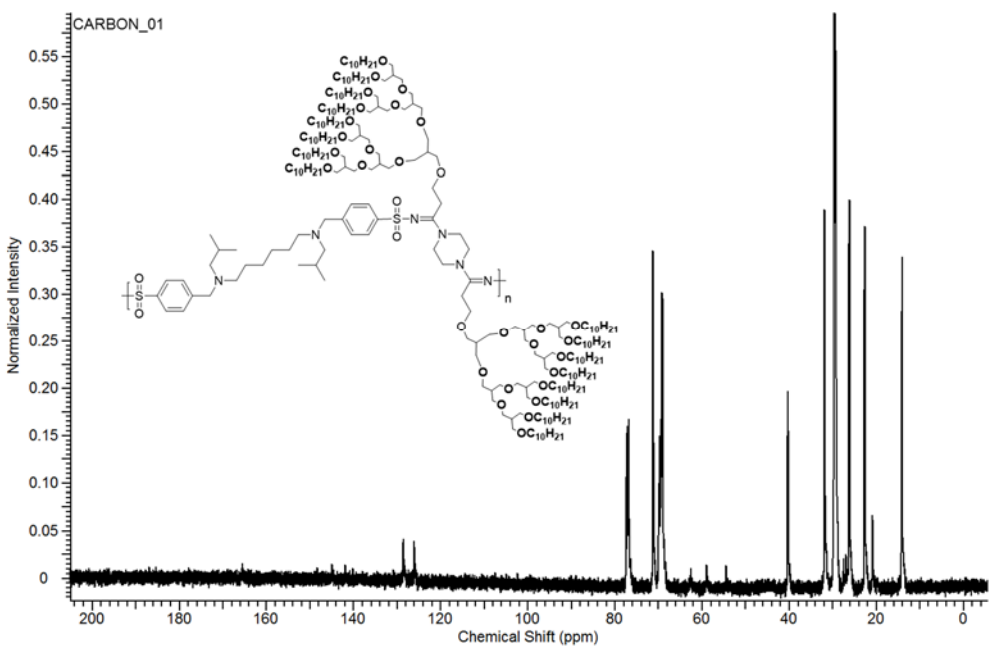
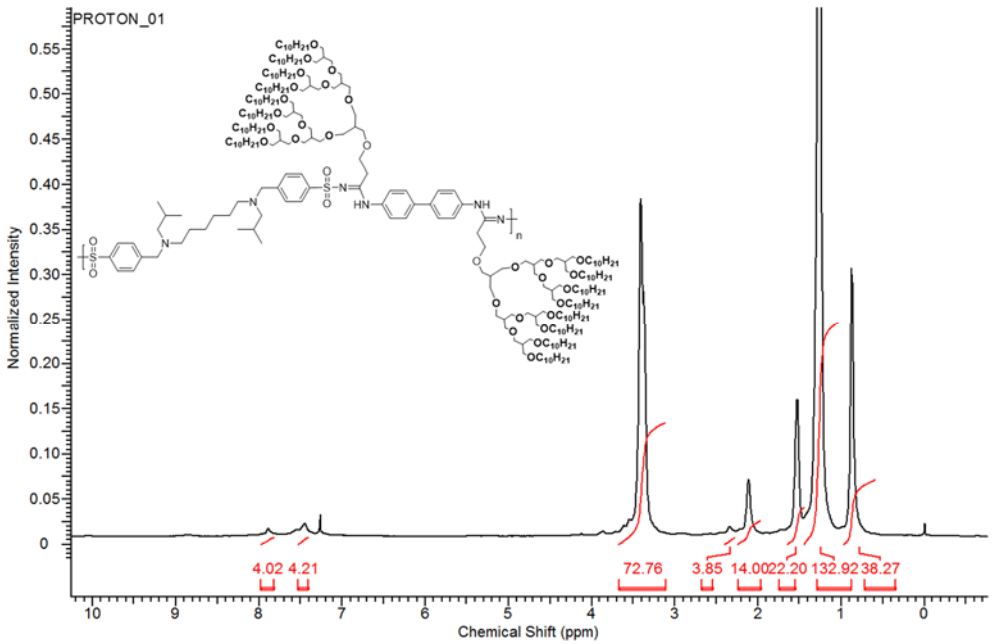


Table Ⅲ-4, entry 29 ($CDCl_3$)



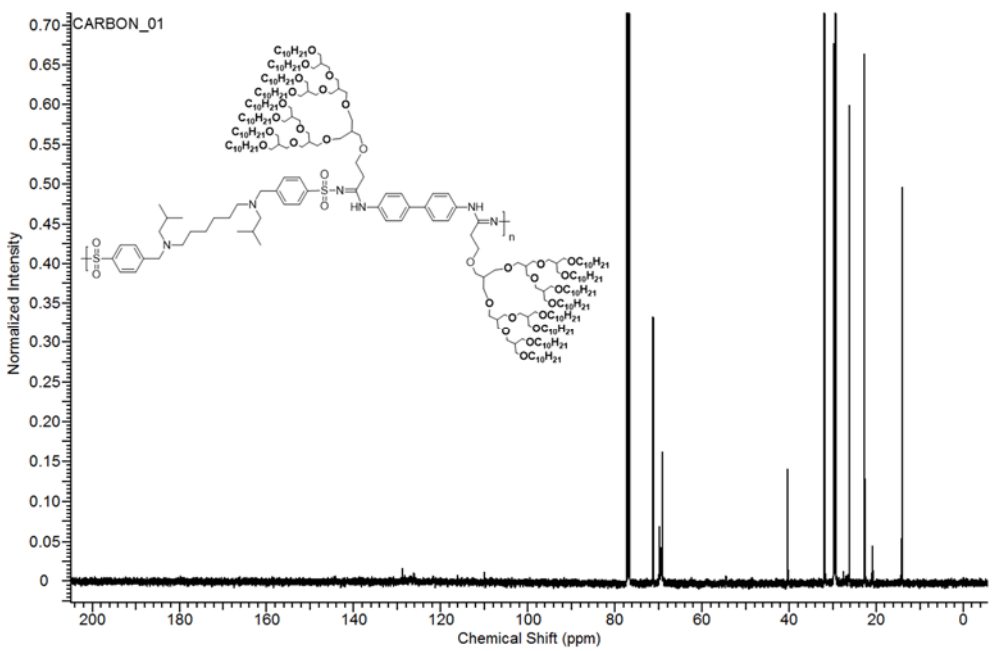
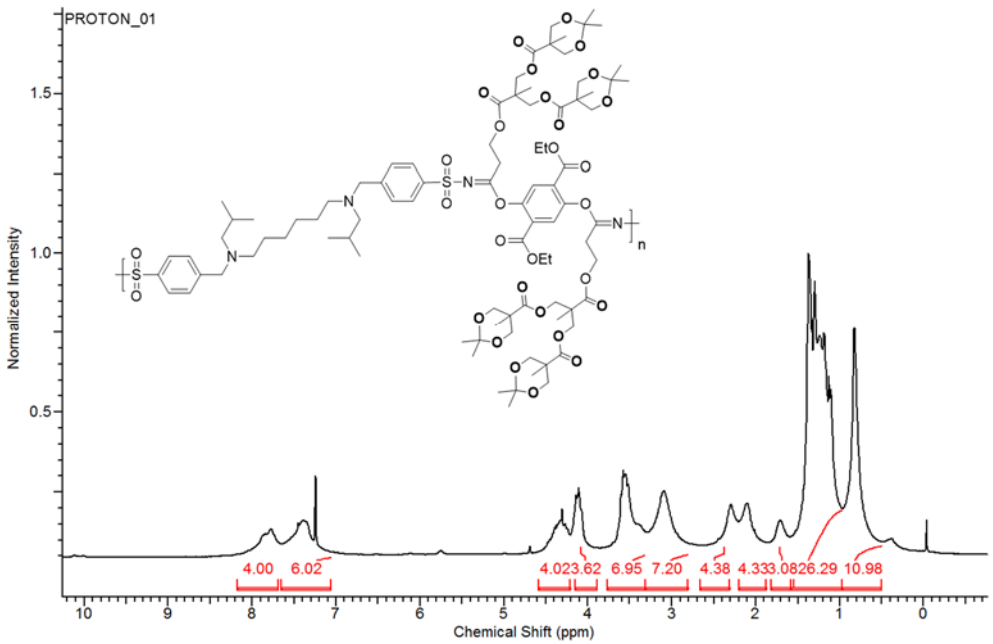


Table Ⅲ-4, entry 30 ($CDCl_3$)



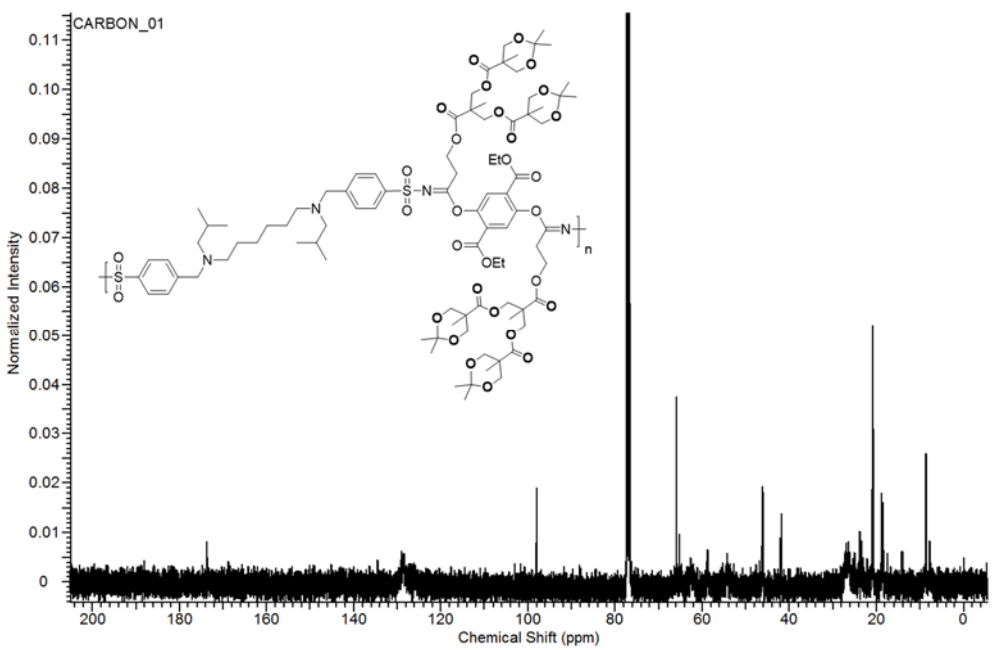
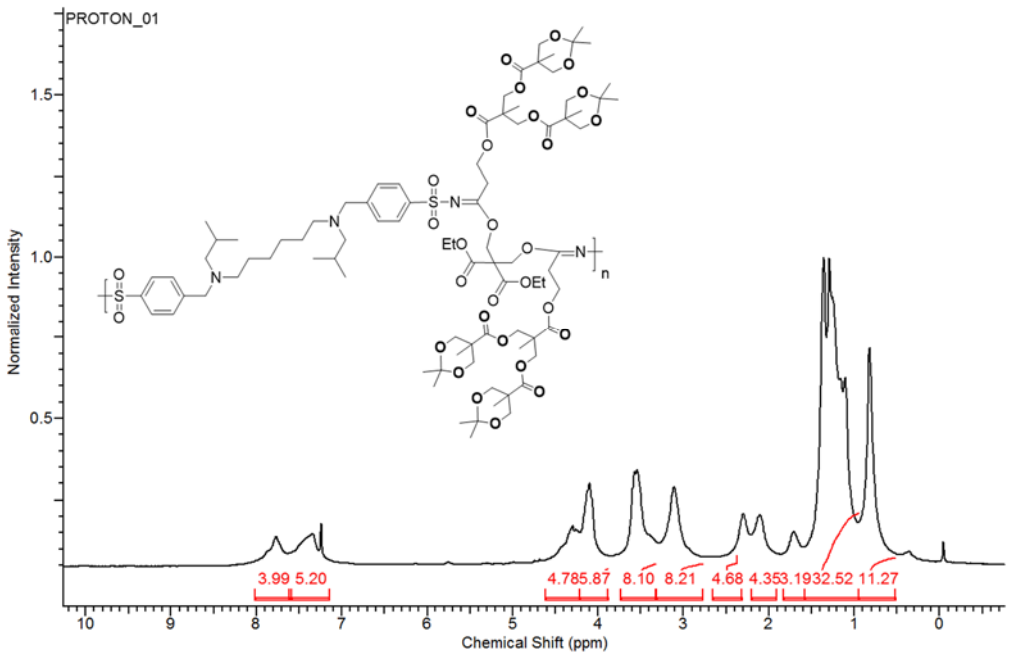


Table Ⅲ-4, entry 31 ($CDCl_3$)



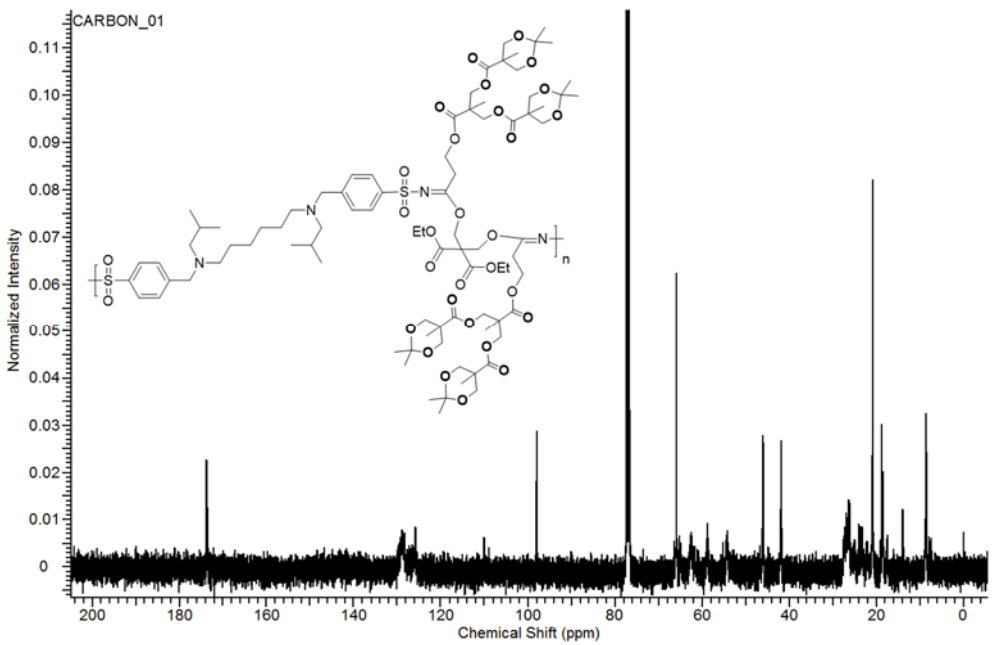
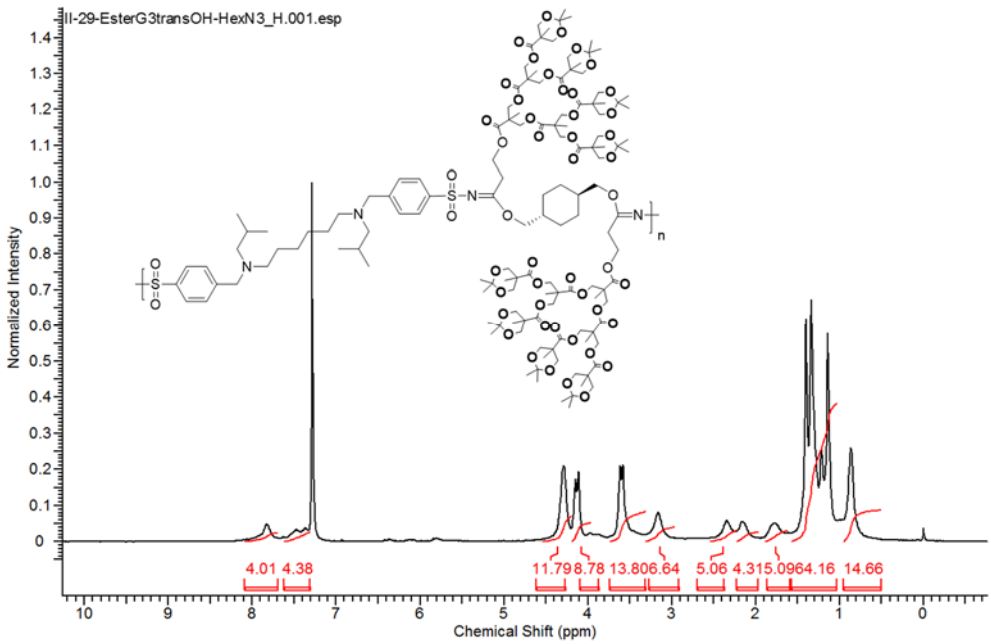


Table Ⅲ-4, entry 32 ($CDCl_3$)



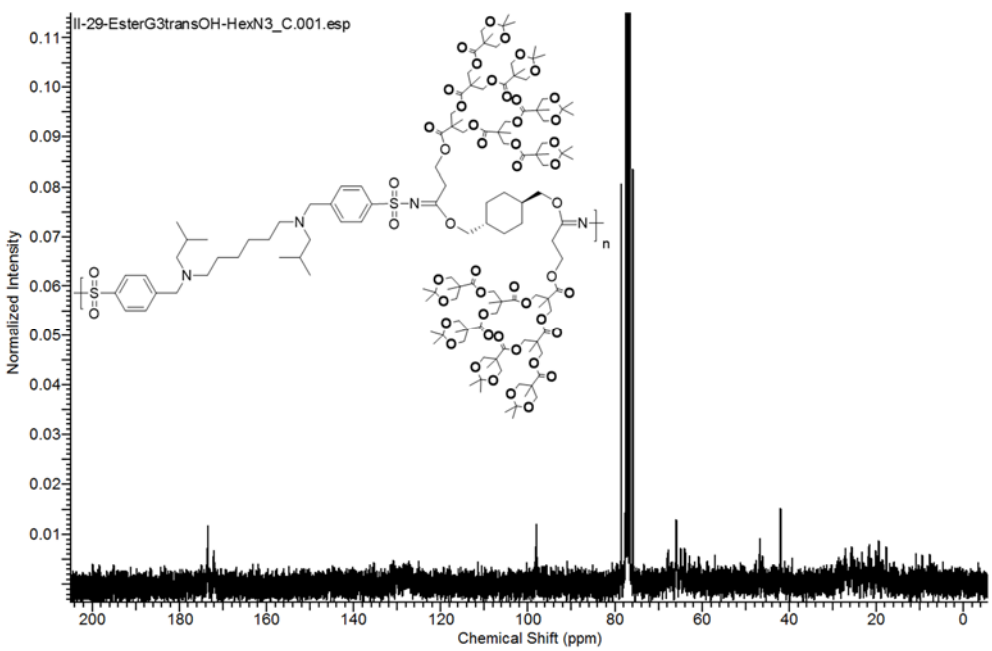
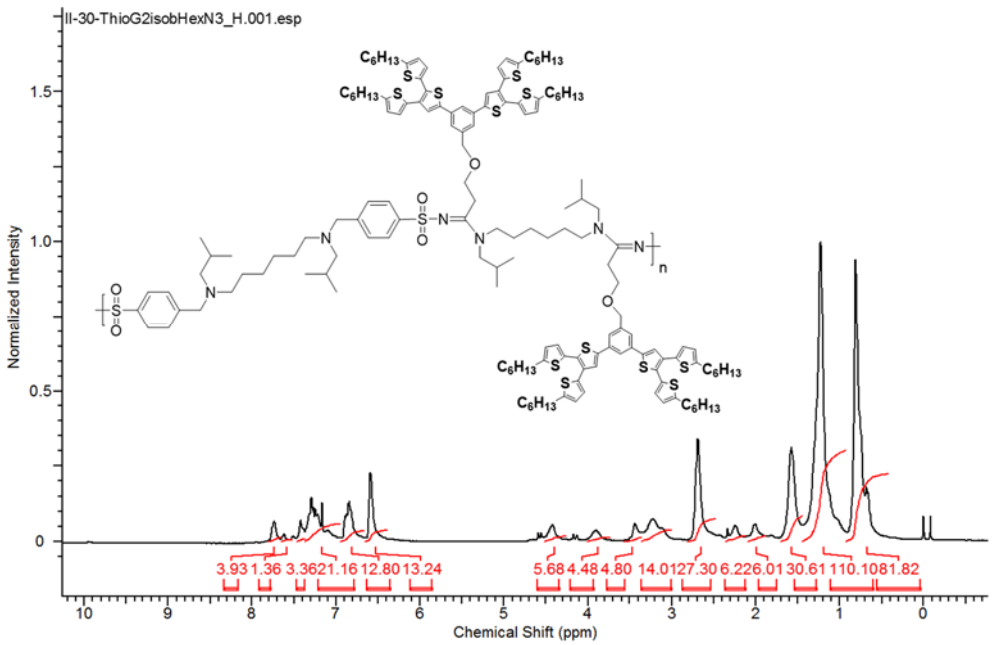


Table Ⅲ-4, entry 33 ($CDCl_3$)



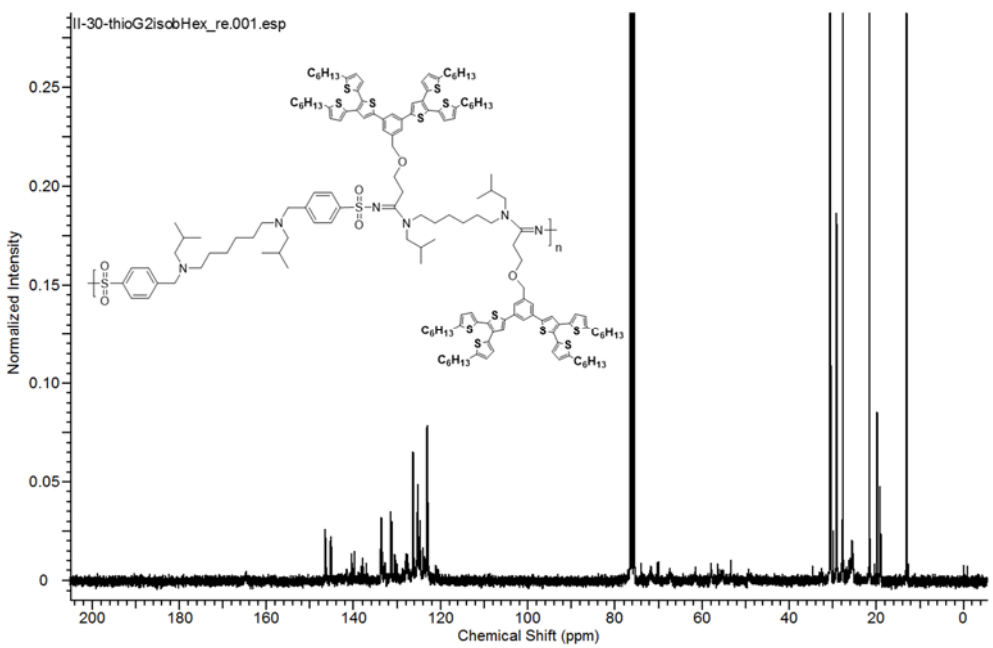
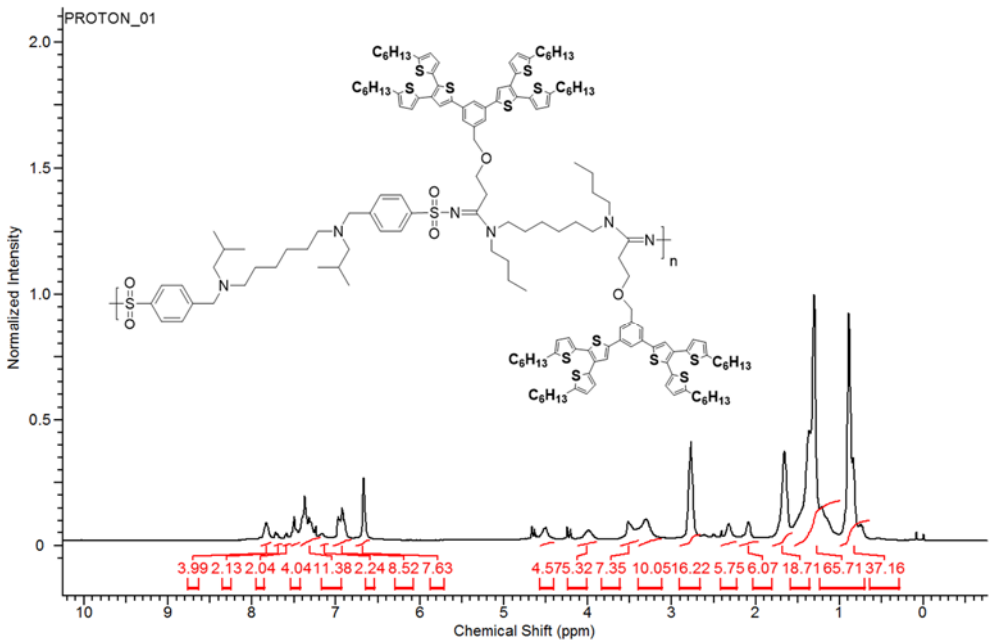


Table Ⅲ-4, entry 34 ($CDCl_3$)



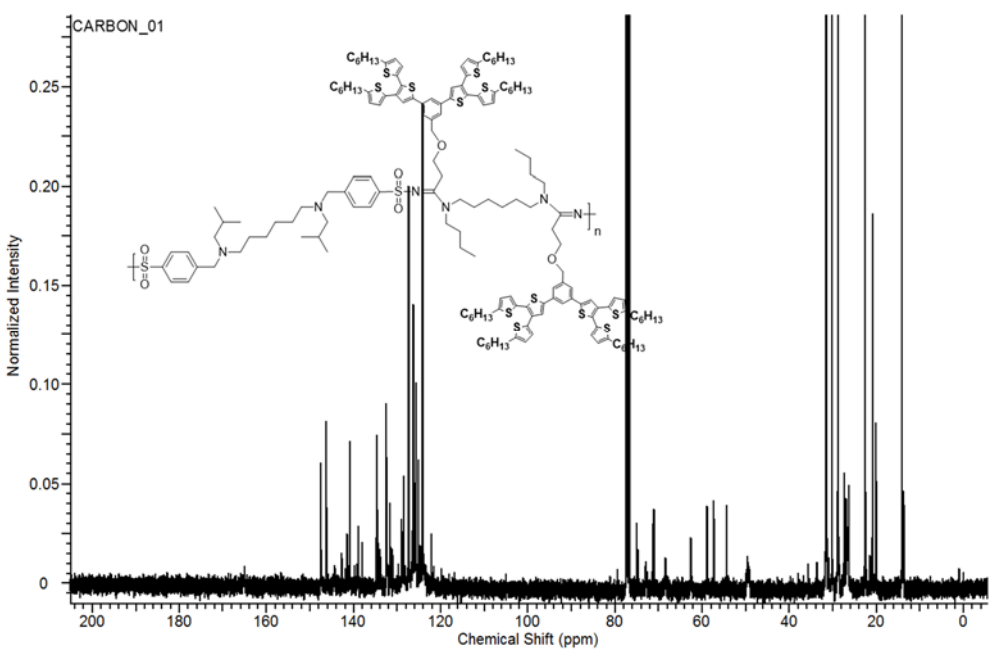
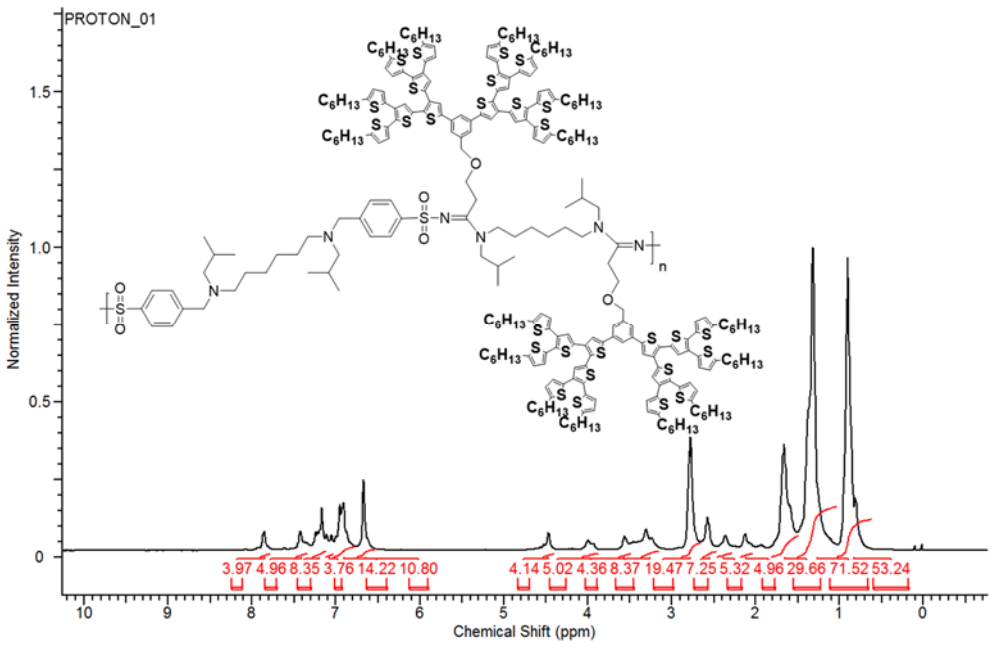


Table Ⅲ-4, entry 35 ($CDCl_3$)



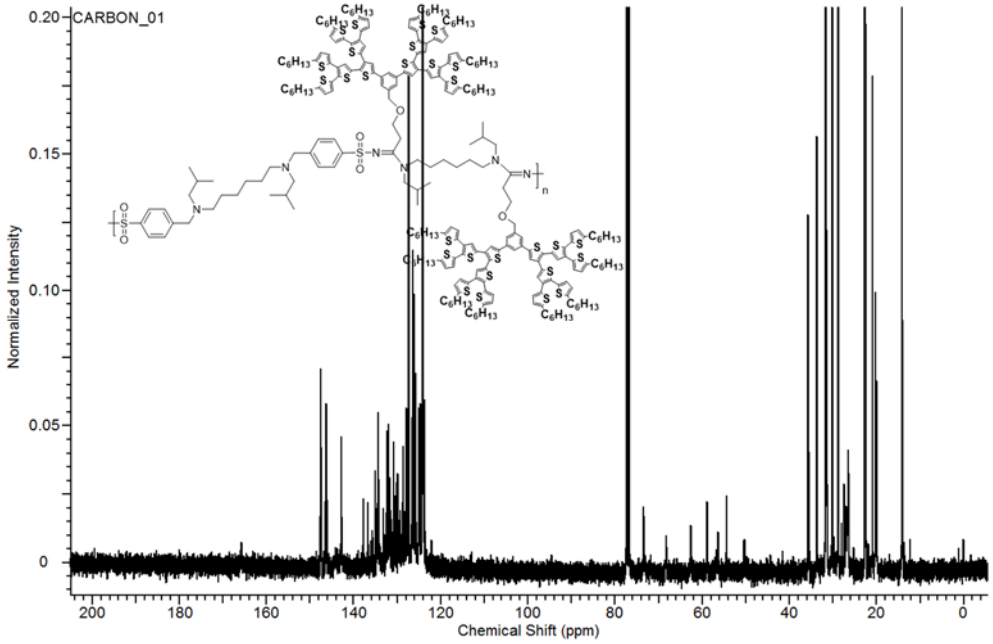
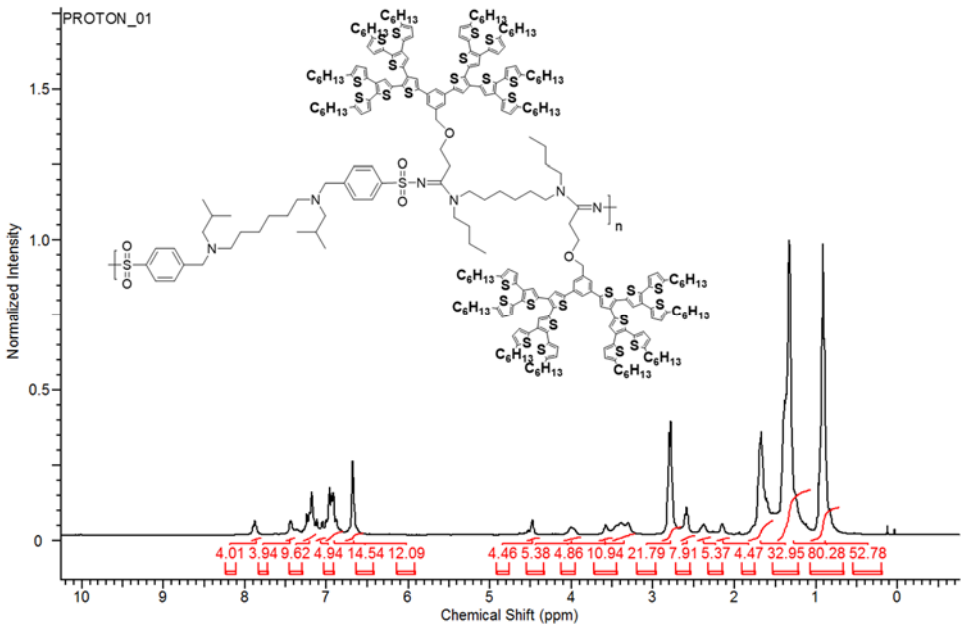
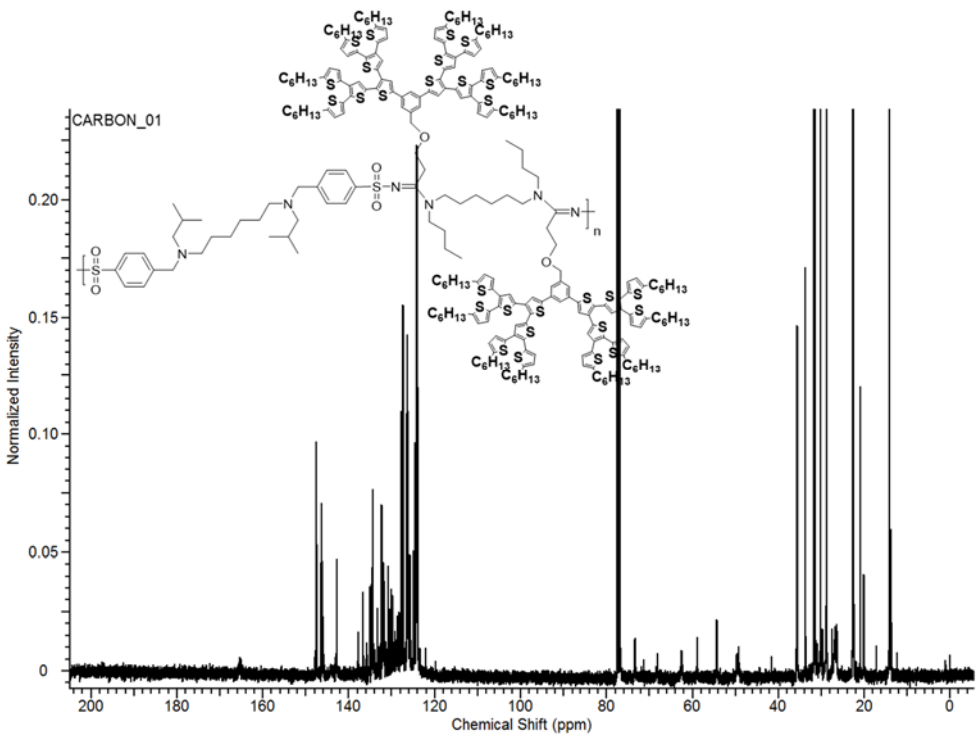


Table Ⅲ-4, entry 36 ($CDCl_3$)





Experimental details

The transmission electron microscopy (TEM) was performed at 120 kV using JEM-2010. The atomic force microscopy (AFM) was performed with a Bruker Nanoscope V Multimode 8 instrument.

Atomic Force Microscopy (AFM) Measurement

The AFM images were collected on a Bruker NanoScope V Multimode 8 device at ambient temperature in tapping mode using non-contact mode silicon tips from Nanoworld (Pointprobe ® tip, NCHR type) with spring constant of 42 N m^{-1} and tip radius of $\leq$ 8 nm.

PS graft polymers were diluted by toluene and Fréchet dendronized polymers were dissolved in THF. All the concentration of the polymer solutions was 0.001 mg/mL. 10 μL of the polymer solutions was dropped on freshly cleaved HOPG by Scotch Tape. Then the HOPG substrate was spin-coated using Spin Coater ACE-200 at a speed 3000 rpm during 30 s. The scanning speed was at a line frequency of 1.0 Hz, and the original images were collected by 8808 EVLR scanner.

Transmission Electron Microscopy (TEM) Measurement

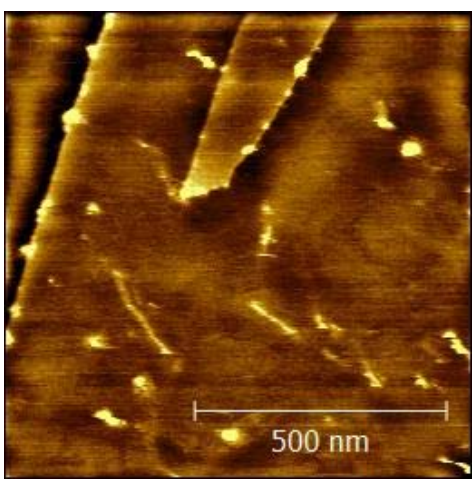
Transmission electron microscopy observation was carried out with a JEOL JEM-2010 operated at 120 kV. The polymer solutions were prepared same conditions with AFM measurement. A drop of the

polymer solution was placed on a carbon-coated copper grid from Electron Microscopy Sciences (Formvar/Carbon 300 Mesh) and spin-coated using Spin Coater ACE-200 at a speed 3000 rpm during 30 s. The staining process to the grid was not necessary.

Direct imaging was carried out with a 120 kV accelerating voltage, using the images acquired with a Dual vision 300 W and SC 1000 CCD camera (Gatan, Inc; Warrendale, PA).

AFM and TEM images of graft and dendrnoized polymers

Table Ⅲ-2, entry 6 (AFM)



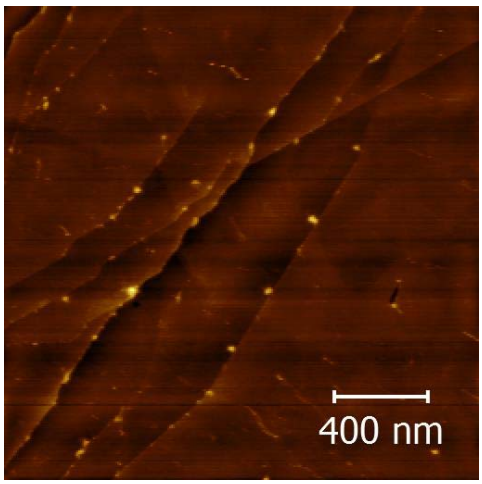
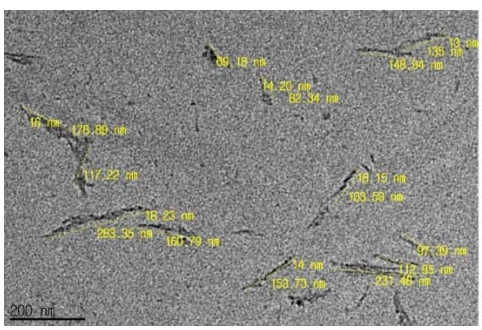
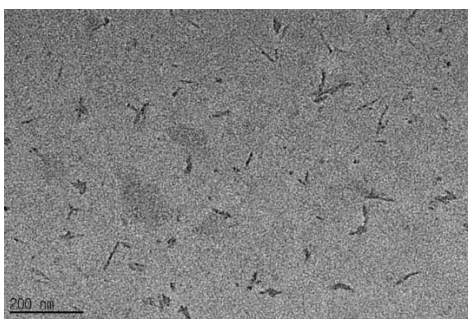
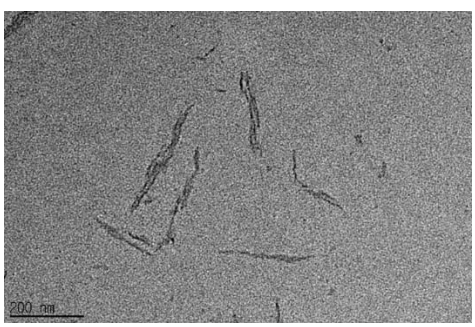


Table Ⅲ-2, entry 6 (TEM)







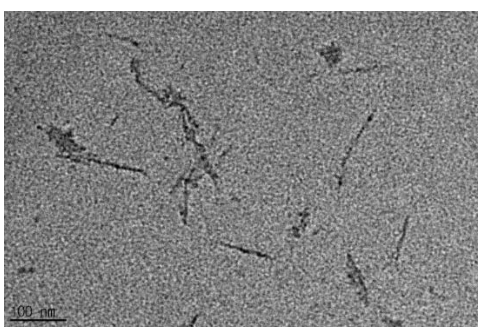


Table Ⅲ-2, entry 7 (AFM)

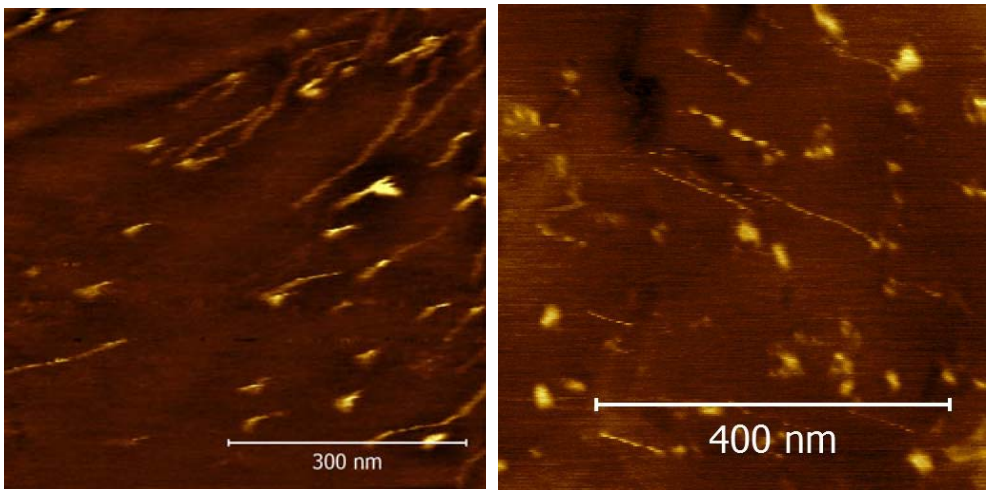


Table Ⅲ-2, entry 7 (TEM)

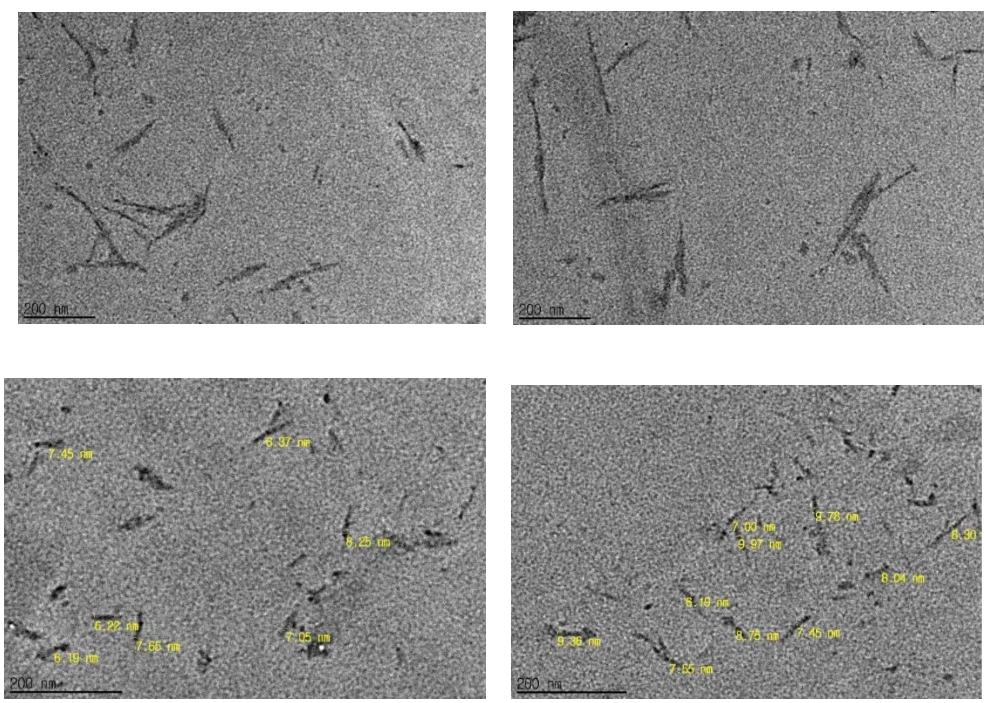
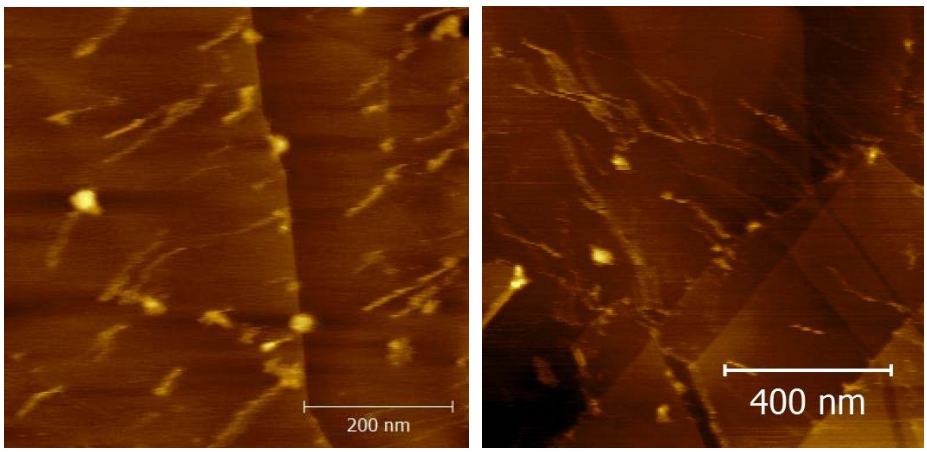


Table Ⅲ-2, entry 8 (AFM)



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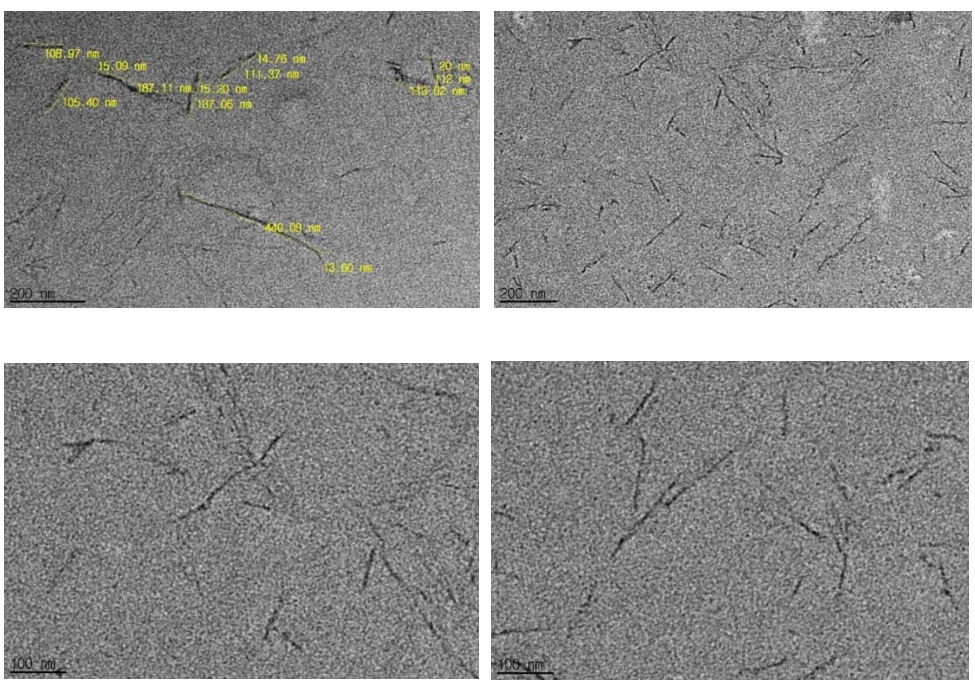


Table Ⅲ-4, entry 9 (AFM)

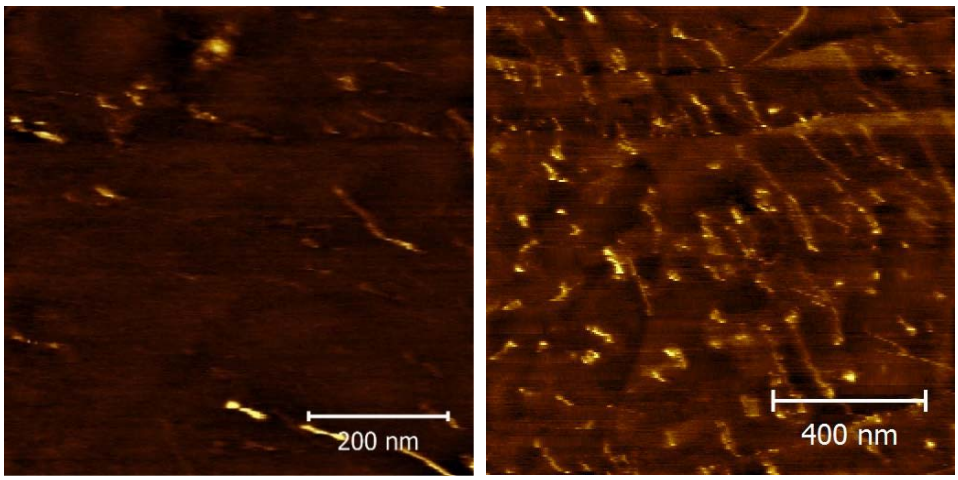


Table Ⅲ-4, entry 9 (TEM)

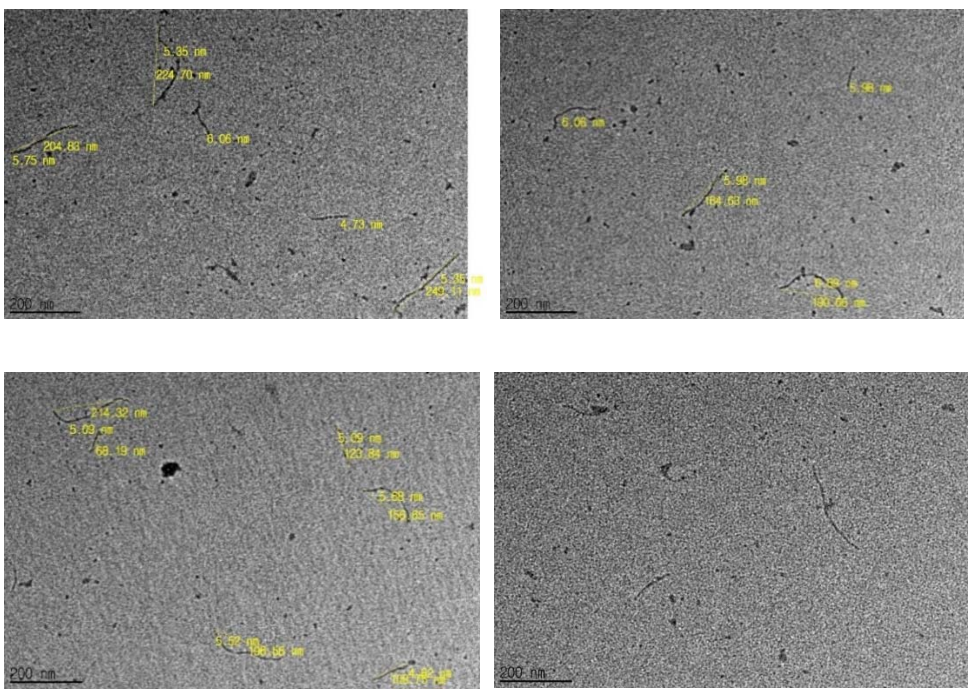


Table Ⅲ-4, entry 10 (AFM)

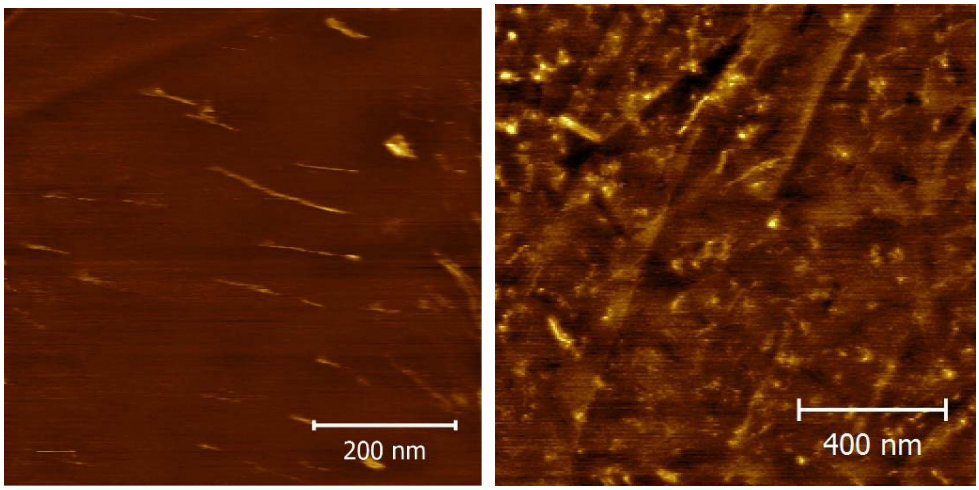


Table Ⅲ-4, entry 10 (TEM)

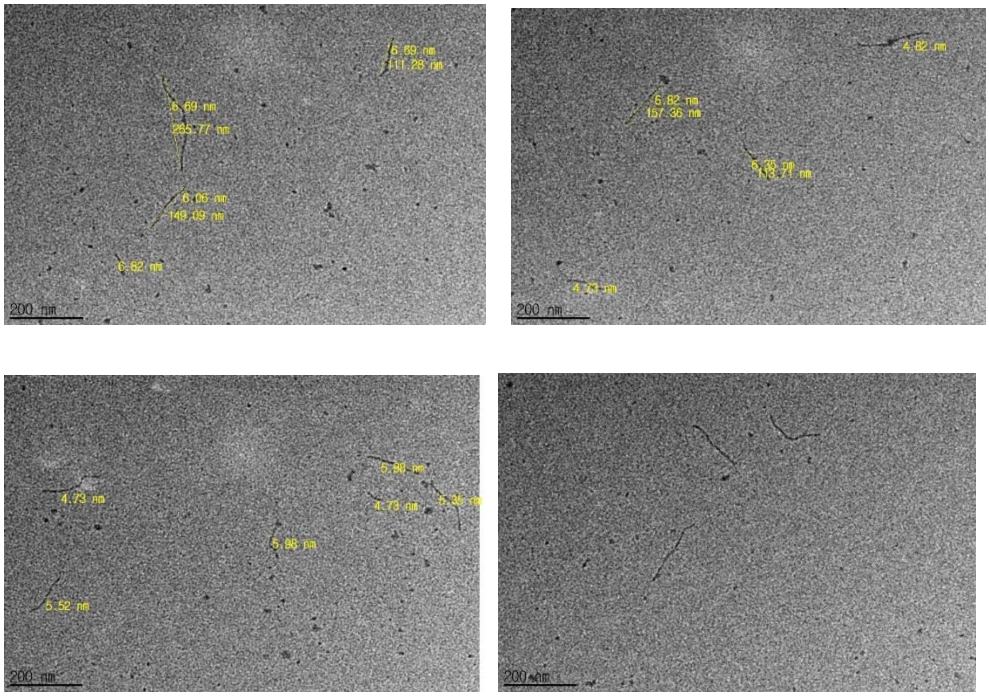
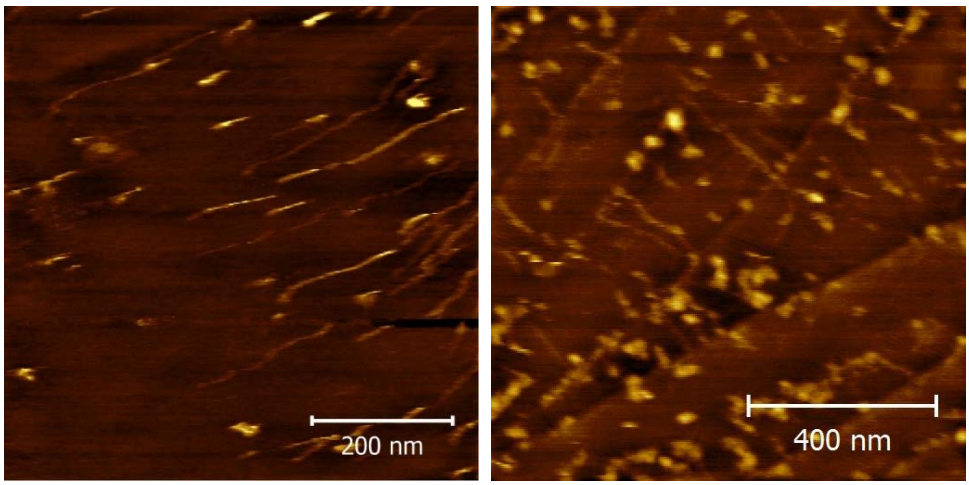


Table Ⅲ-4, entry 11 (AFM)



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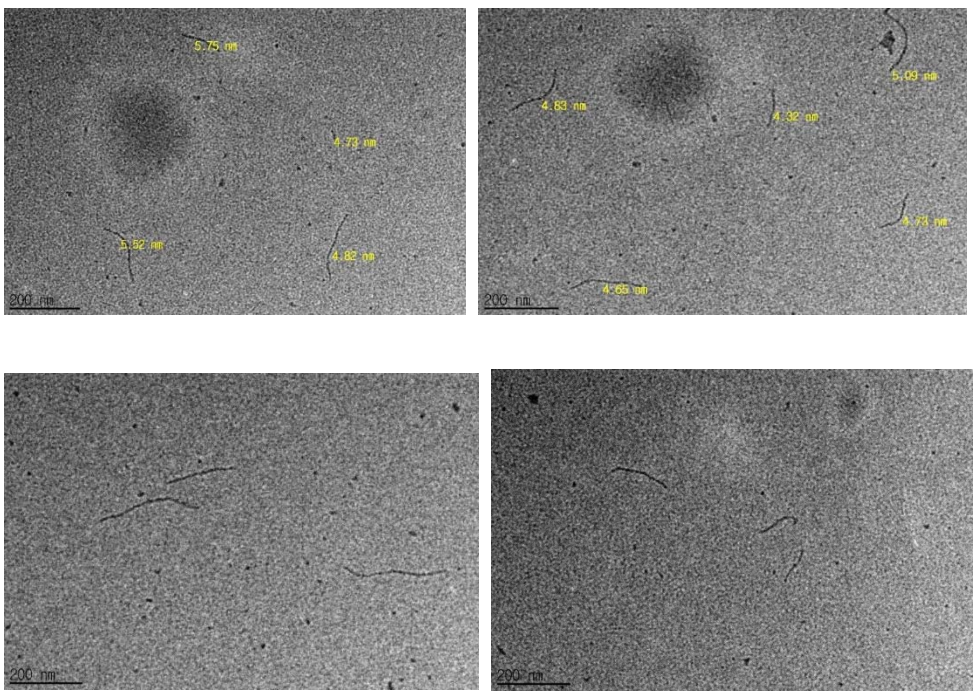
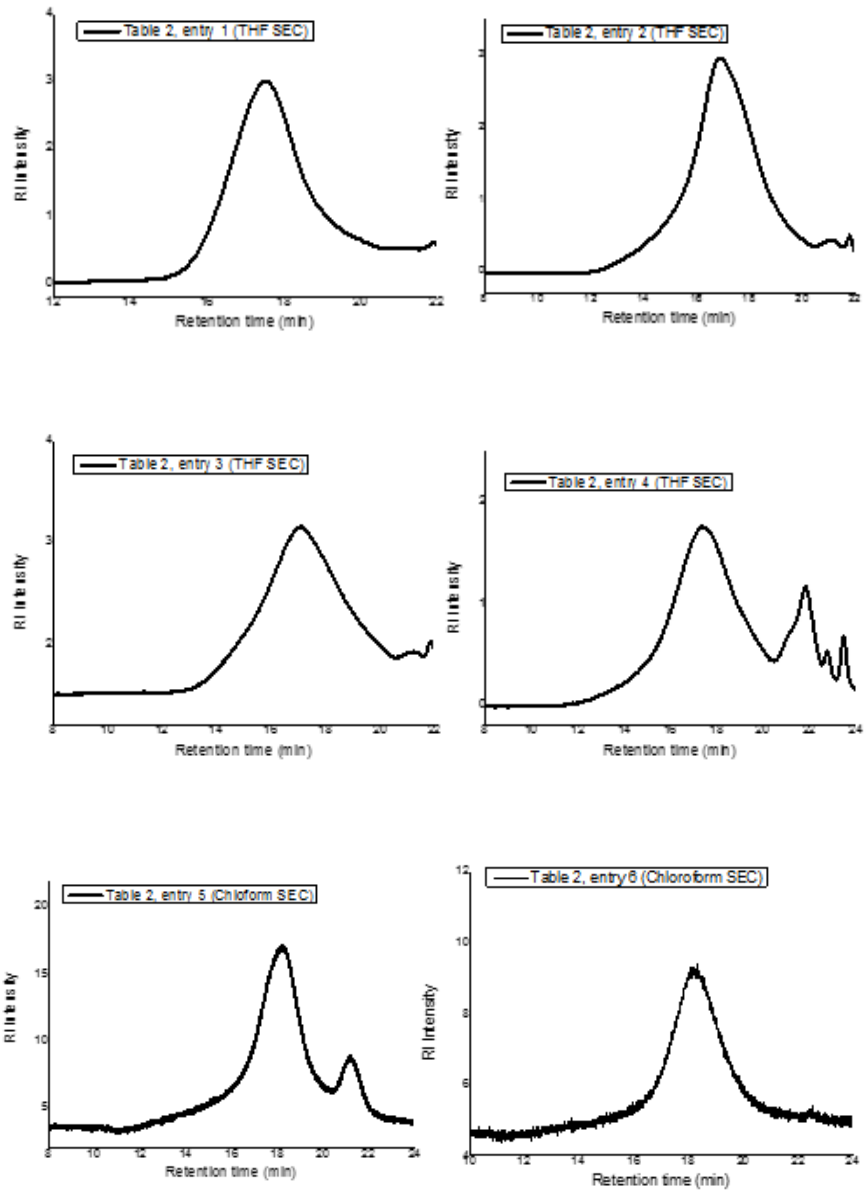


SEC traces of various graft polymers



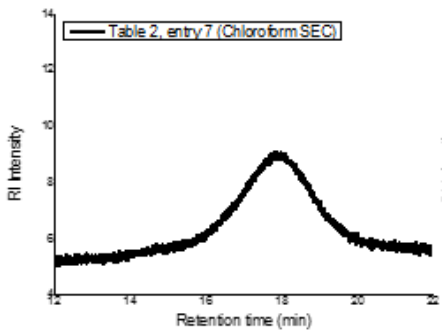


Table 2, entry 7 (Chloroform SEC)
RI Intensity
Retention time (min)

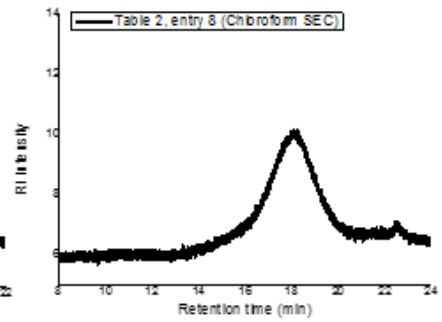


Table 2, entry 8 (Chloroform SEC)
RI Intensity
Retention time (min)

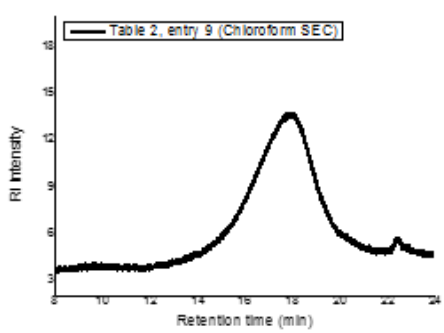


Table 2, entry 9 (Chloroform SEC)
RI Intensity
Retention time (min)

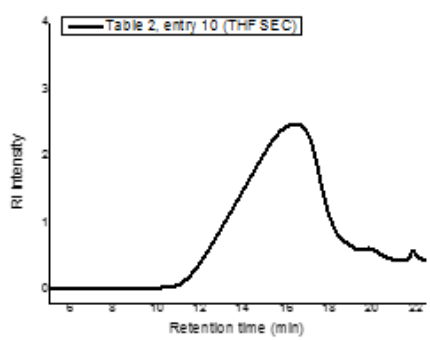
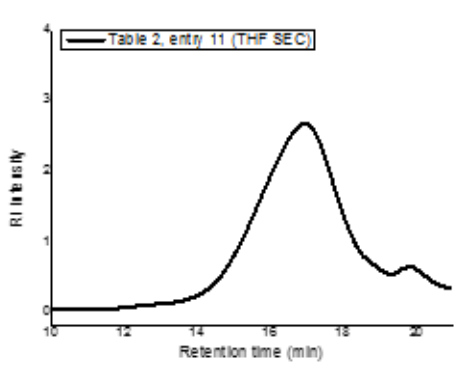


Table 2, entry 10 (THF SEC)
RI Intensity
Retention time (min)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RI Intensity
Retention time (min)

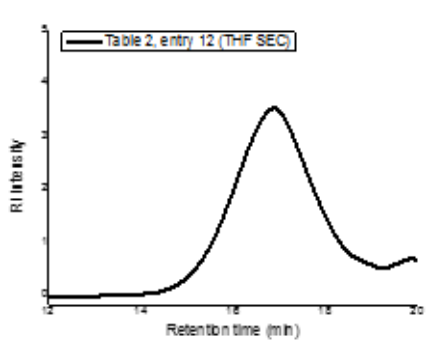


Table 2, entry 12 (THF SEC)
RI Intensity
Retention time (min)

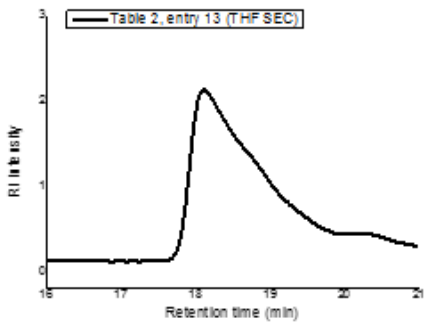
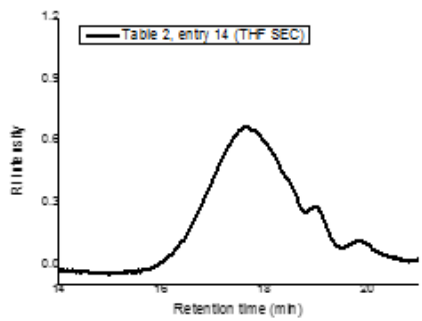


Table 2, entry 13 (THF SEC)
RI Intensity
Retention time (min)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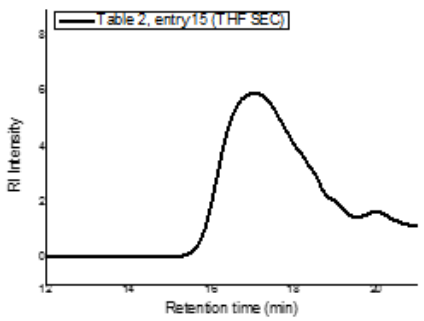


Table 2, entry15 (THF SEC)
RI Intensity
Retention time (min)

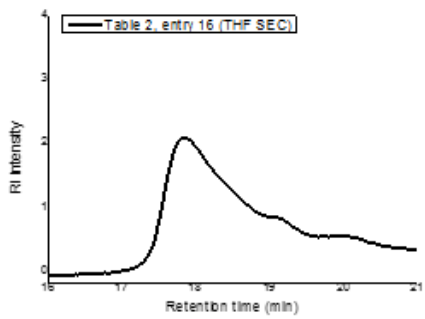
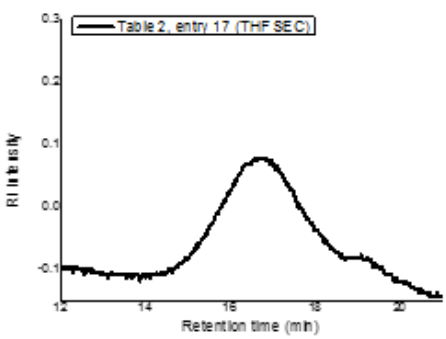


Table 2, entry 16 (THF SEC)
RI Intensity
Retention time (min)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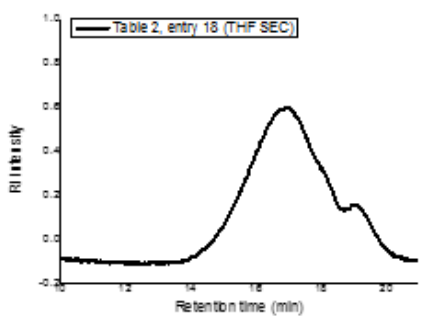
RI Intensity
Retention time (min)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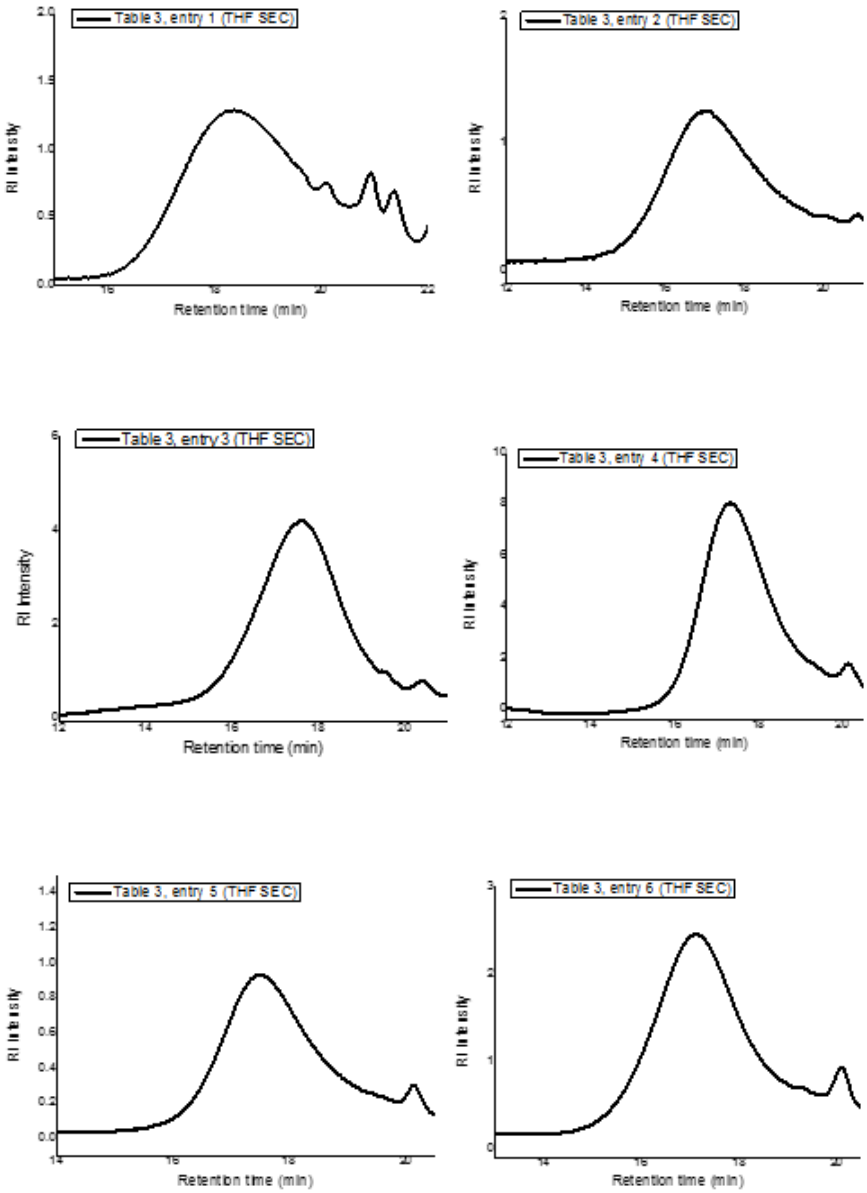
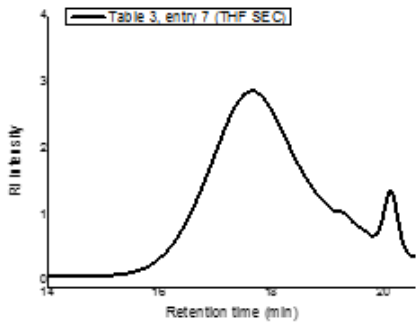
RI Intensity
Retention time (min)

SEC traces of various dendronized polymers

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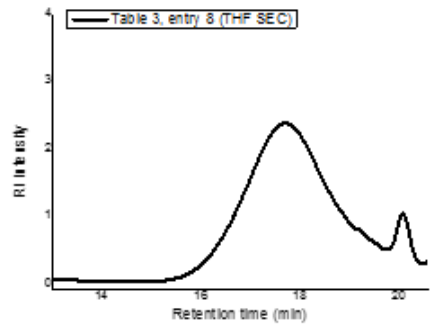
Retention time (min)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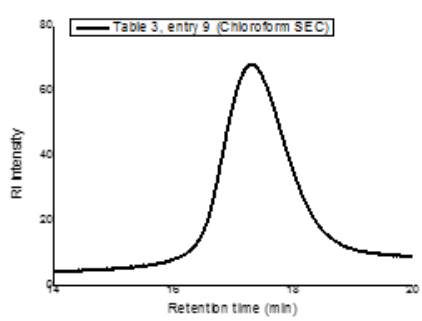
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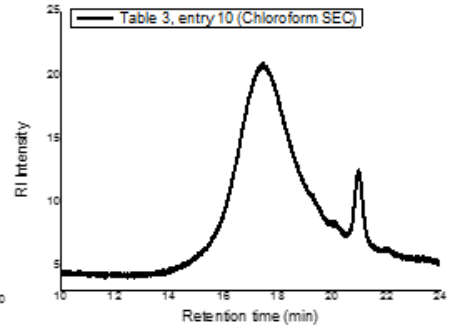
Retention time (min)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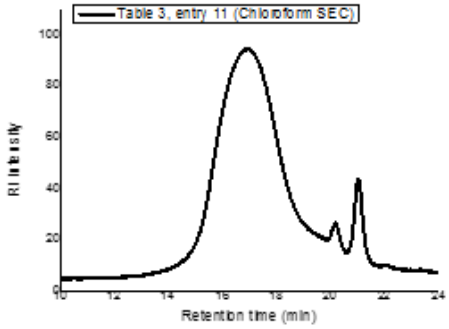
Retention time (min)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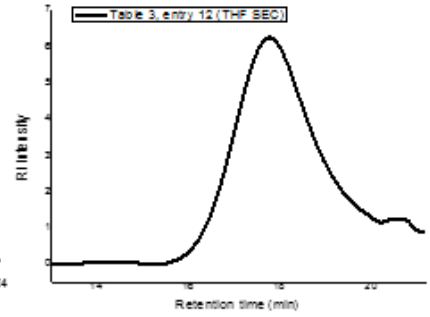
Retention time (min)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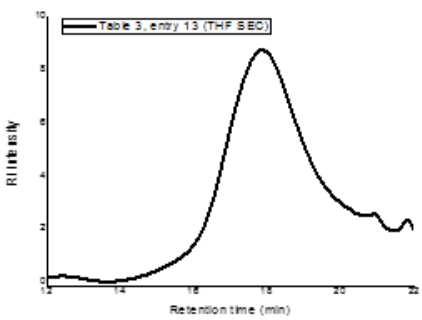
Retention time (min)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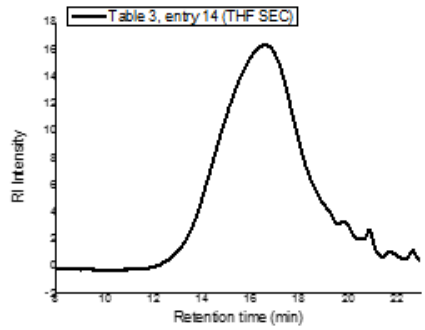
Retention time (min)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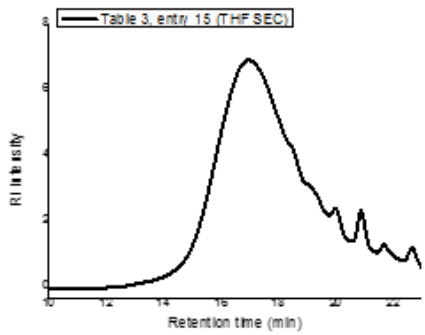
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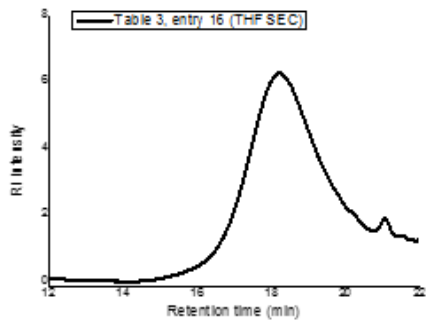
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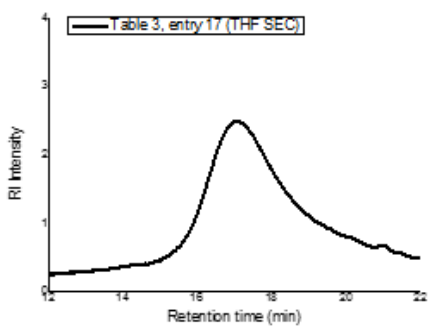
Retention time (min)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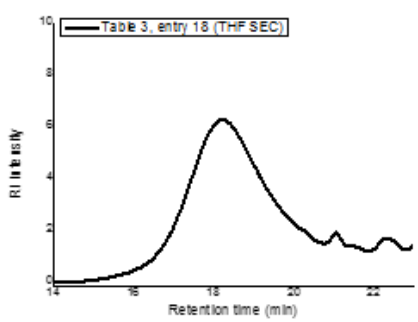
Retention time (min)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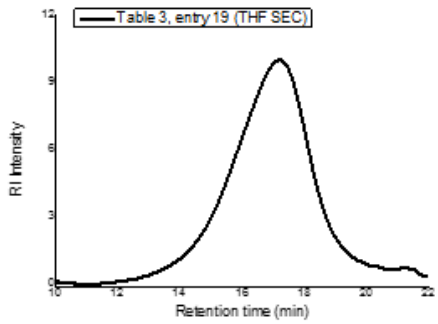
RI Intensity
Retention time (min)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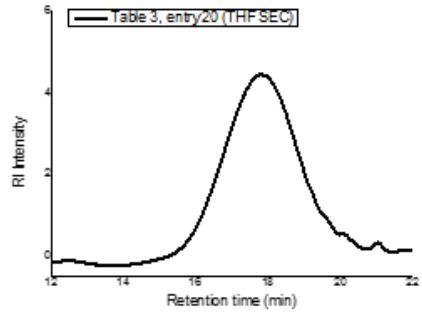
Retention time (min)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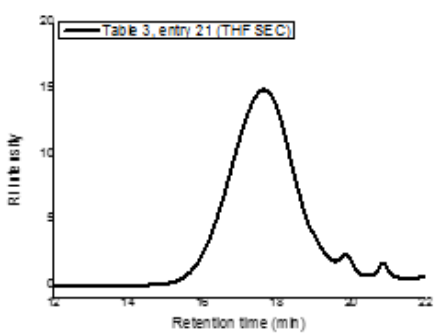
Retention time (min)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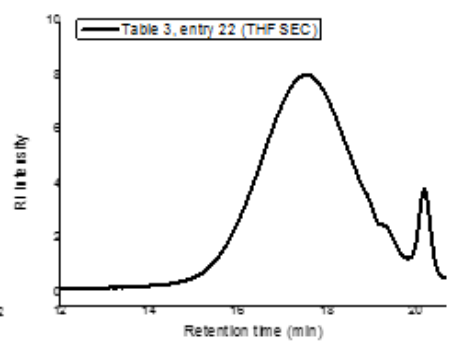
Retention time (min)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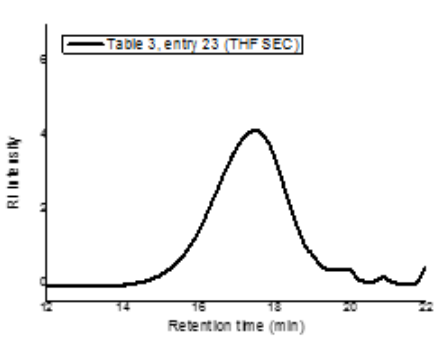
Retention time (min)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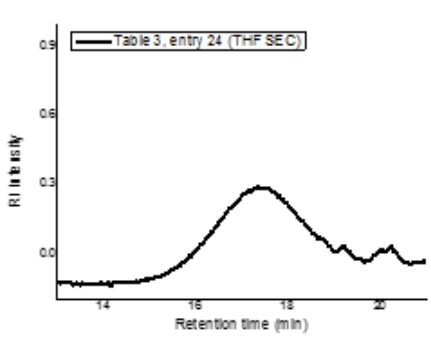
Retention time (min)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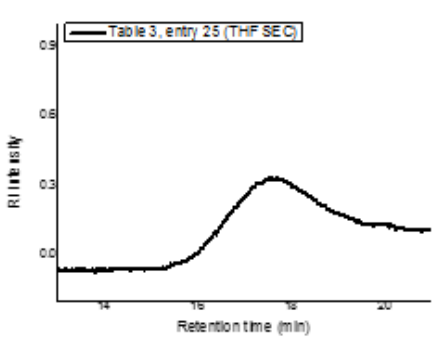
Retention time (min)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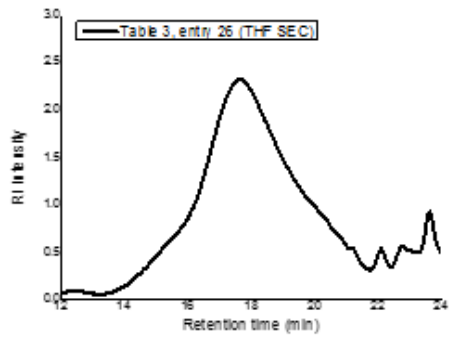
RI Intensity
Retention time (min)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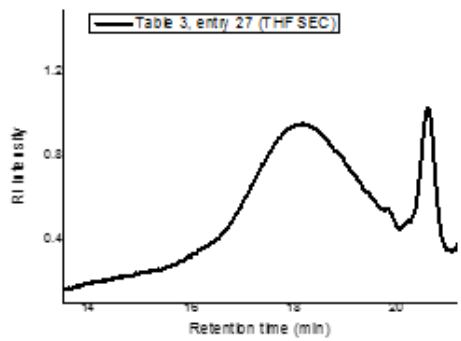
RI Intensity
Retention time (min)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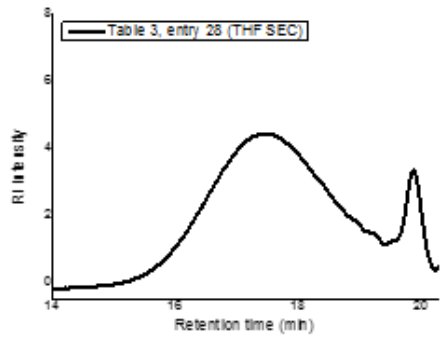
RI Intensity
Retention time (min)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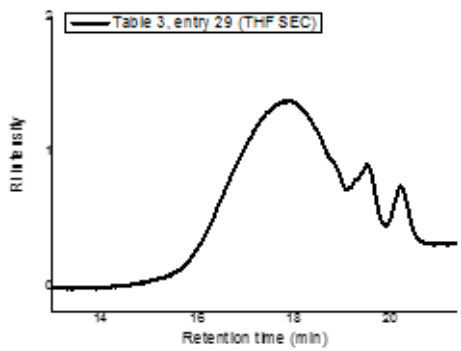
RI Intensity
Retention time (min)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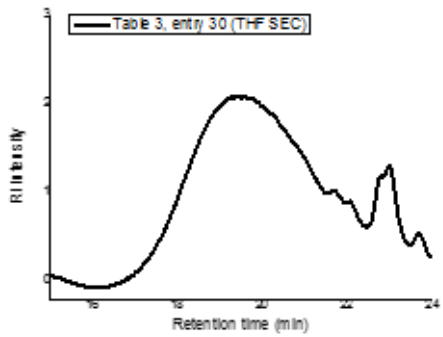
Retention time (min)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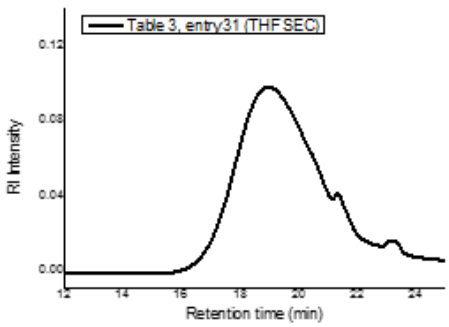
RI Intensity
Retention time (min)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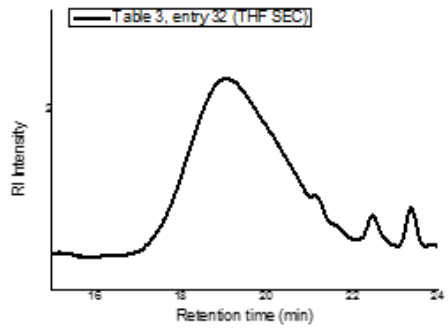
Retention time (min)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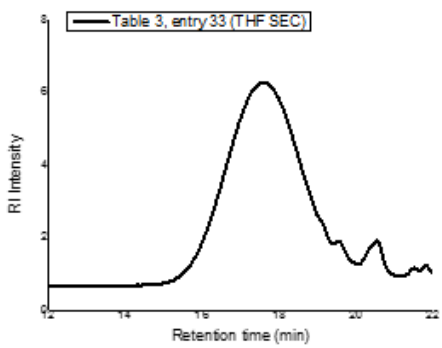
Retention time (min)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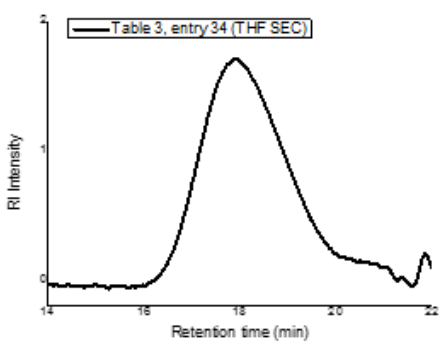
Retention time (min)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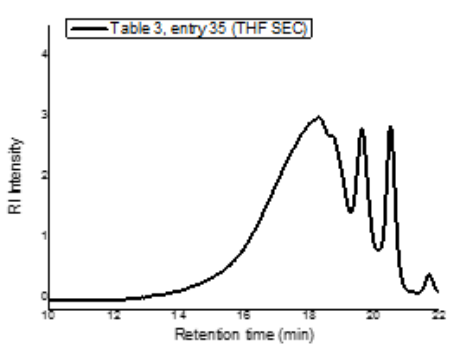
Retention time (min)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RI Intensity
Retention time (min)

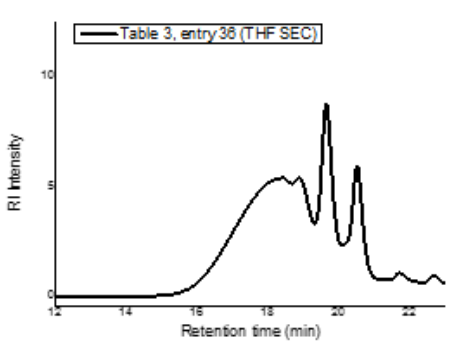
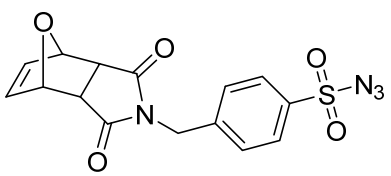


Table 3, entry36 (THF SEC)
RI Intensity
Retention time (min)

Chapter Ⅳ - Experimental

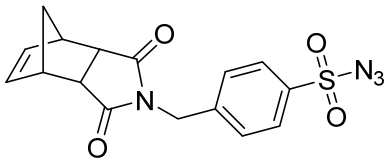
Synthetic procedure for bis-sulfonyl azide

4-(((3aR,4R,7S,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)methyl)benzenesulfonyl azide : (oxanorbornene sulfonyl azide)



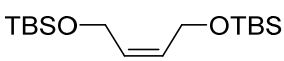
: To a stirred solution of imide form of oxanorbornene (10 mmol, 1.0 eq) and potassium carbonate (20mmol, 2.0eq) in acetonitrile and water mixture (9 : 1), 4-(bromomethyl)benzenesulfonyl chloride (**1**) (12 mmol, 1.2 eq) was added and stirred for 12h at room temperature. After extraction with ethyl acetate twice, the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatograph on silica gel (hexane : EA = 10 : 1), affording oxanorbornene sulfonyl azide as a white solid (6.3mmol, yield of 63%).

4-(((3aR,4S,7R,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)methyl)benzenesulfonyl azide



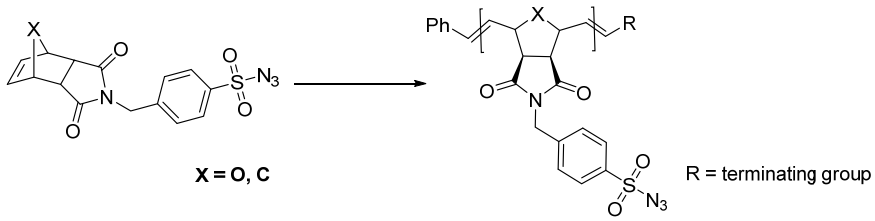
: To a stirred solution of imide form of exo-norbornene (10 mmol, 1.0 eq) and potassium carbonate (20mmol, 2.0eq) in acetonitrile and water mixture (9 : 1), 4-(bromomethyl)benzenesulfonyl chloride (12 mmol, 1.2 eq) was added and stirred for 12h at room temperature. After extraction with ethyl acetate twice, the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatograph on silica gel (hexane : DCM = 9 : 1), affording oxanorbornene sulfonyl azide as a tinted yellow solid (7.2mmol, yield of 72%).

(Z)-2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodec-6-ene



: To a stirred solution of (Z)-but-2-ene-1,4-diol (10 mmol, 1.0 eq) in *N,N*-dimethylformamide, imidazole (50mmol, 5.0eq) and TBSCl (30 mmol, 3 eq) was added and stirred for 8h at room temperature. After quenching with saturated solution of $NaHCO_3$ (aq) and extraction with DCM twice, the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatograph on silica gel, affording colorless liquid. (9.8mmol, 98%)

Polymerization procedure for sulfonyl azide polymer



: To a stirred solution of exo-norbornene derivatives containing sulfonyl azide (0.3 mmol, 1.0 eq) in DCM (0.1 M), Grubbs catalyst 3rd generation (0.01mmol, M/I=30) in DCM was added to initiate polymerization at room temperature under Ar atmosphere. After 3min, excess amount of terminating agent was added and stirred for 6h. The crude mixture was precipitated into MeOH, which afforded pale brown solid.

General polymerization procedure for multi-graft polymer

: Sulfonyl azide prepolymer (1 eq), mono-functionalized alkyne macromonomer (1.1 eq), mono-functionalized amine macromonomer (1.1 eq) and 10 mol% of CuCl was added to reaction flask and purged with Ar atmosphere 3 times. And then degassed DCM and TEA (5 eq) was added. The polymerization underwent at RT for 18 h under Ar atmosphere. The resulting mixture was precipitated into selected solvent. The resulting polymers were dissolved in $CHCl_3$ and passed through the short neutral alumina column to remove the residual copper. Then, those were precipitated again into selected solvent to ensure complete removal of monomers, and dried under vacuum.

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국문초록

잘 정의된 고분자 구조를 간단한 방법으로 구축하는 것은 모든 합성화학자들의 지향점이다. 특히 멀티컴포넌트 고분자 중합 분야에서는 모노머 간의 완벽한 독립성이 확보되기 힘들기 때문에 결함 없는 고분자를 만들기가 매우 어렵다. 본 논문의 세 개의 챕터는 구리 촉매를 이용한 성공적인 멀티컴포넌트 중합법을 다루고 있으며, 간단한 합성 방법으로 높은 선택성을 가지고 매우 높은 효율로 고분자를 합성할 수 있음을 소개하고 있다.

챕터 2는 3가지 단량체 (diyne, sulfonyl azides, and diols)를 이용하여 poly(*N*-sulfonylimidates)의 다양한 라이브러리 고분자 합성을 보고하고 있다. 본 합성법을 이용하여 매우 간단히 세 가지 단량체 중 한 종류를 달리함으로써 새로운 고분자를 합성할 수 있다. 또 합성된 고분자 (polyimidates)는 일반적인 click반응을 넘어서 매우 선택적인 반응성을 보이며 기존의 멀티컴포넌트 중합이 가지는 좁은 범위의 단량체 후보군과 낮은 분자량을 가지는 고분자의 생성을 극복하였다. 나아가 손쉽게 접할 수 있고 상온에서 안정적인 diol을 고분자 합성에 적용시킴으로써, 본 합성법은 멀티컴포넌트 고분자를 만들기 위한 단량체 간의 수많은 조합을 가능하게 하였다는 점에서 의의가 있다.

챕터 3은 구리촉매를 이용한 멀티컴포넌트 중합법을 통해 다양한 그라프트 중합체와 덴드론화 중합체의 효율적이고 경제적인 합성법을 다루고 있다. 이 챕터에서 우리는 두 가지의 고분자

(polyamidines 과 polyimidates) 합성체계를 통합하여 구성 단량체 간의 완벽한 독립성을 확보하였고 고차원적인 고분자 합성으로 확장시켰다. 11가지의 diamine과 3가지의 diol, 6가지의 bis-sulfonyl azide, 그리고 14가지의 macromonomer (4가지의 선형 고분자와 10가지의 덴드론)의 조합을 통해 54가지의 서로 다른 높은 분자량의 그라프트 중합체와 덴드론화 중합체를 합성할 수 있었다. 이 방법을 통해 one-shot 반응으로 복잡한 구조의 고분자를 간단히 합성하였으며 고분자의 주 사슬과 보조 사슬을 동시에 조절할 수 있음이 가능함을 보였다.

챕터 4에서는 graft-to 전략을 이용하여 다중-그라프트 중합체의 합성에 대해 다루고 있다. 본 방법론을 사용하여 한 고분자 내에 서로 다른 보조 사슬이나 덴드론들을 동시에 접목시킬 수 있다. 두 가지의 다른 mono-functionalized macromonomer 들은 고분자의 구조와 특성, 물성을 더욱 다양하고 풍성하게 만들어 줄 것으로 예상하며 미래 기능성 고분자의 손쉬운 합성의 기틀을 마련할 것임을 예측해본다.

주요어 : 구리촉매를 이용한 멀티컴포넌트 중합, 라이브러리 고분자 합성, one-shot 합성, 그라프트 중합체, 덴드론화 중합체
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